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Field Evaluation of Solvent-Free Sampling with Di-n-butylamine for the Determination of Airborne Monomeric and Oligomeric 1,6-Hexamethylene Diisocyanate

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FIELD EVALUATION OF SOLVENT-FREE SAMPLING WITH DI-*N*-BUTYLAMINE FOR THE DETERMINATION OF AIRBORNE MONOMERIC AND OLIGOMERIC 1,6-HEXAMETHYLENE DIISOCYANATE

THESIS

Tiffany R. Heline, Captain, USAF

AFIT-ENV-14-M-29

DEPARTMENT OF THE AIR FORCE
AIR UNIVERSITY

AIR FORCE INSTITUTE OF TECHNOLOGY

Wright-Patterson Air Force Base, Ohio

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THESIS

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In Partial Fulfillment of the Requirements for the

Degree of Master of Science in Industrial Hygiene

Tiffany R. Heline, BS

Captain, USAF

March 2014

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Abstract

The purpose of this research was to perform a field evaluation of a new solvent-free sampling method using di-*n*-butylamine for the determination of airborne monomeric and oligomeric 1,6-hexamethylene diisocyanate (HDI). During this study, the Supelco ASSET™ EZ4-NCO Dry Sampler was compared to the Omega Specialty Instrument Company ISO-CHEK® sampler. Three specific questions were addressed: 1) can HDI oligomers be quantified using liquid chromatography and mass spectrometric detection (HPLC-MS); 2) do ASSET™ and ISO-CHEK® samplers collect equivalent HDI monomer and oligomer concentrations; and 3) what is the relative cost of ASSET™ samplers verse ISO-CHEK® for employee monitoring in the US Air Force.

Side-by-side HDI air sampling was conducted during polyurethane spray painting operations to determine if there was a significant difference between ISO-CHEK® and ASSET™ samplers. ASSET™ samplers were analyzed by HPLC-MS for HDI monomer and oligomers, including HDI biuret and isocyanurate. The ASSET™ sampler (n = 32) collected significantly higher levels of HDI monomers (mean difference = 0.029 mg m^{-3}), indicating ISO-CHEK® samplers potentially underestimate true HDI monomer exposures. HDI oligomer results were inconclusive. Finally, the analytical cost for the ASSET™ sampler was determined to be 50 percent less than ISO-CHEK® resulting in a cost savings of $32 K over 5 years.

Acknowledgments

I would like to acknowledge the assistance of my advisor, Lieutenant Colonel (Dr.) Dirk Yamamoto, for his patience, motivation, and enthusiasm through the graduate program and thesis process. My gratitude is also extended to Dr. Daniel Felker, under his tutelage I learned to operate and develop a love-hate relationship with the HPLC-MS. To Dr. Mitchell Rubenstein, thank you for your subject matter expertise and endless passion for isocyanate research. To Lieutenant Colonel (Dr.) LeeAnn Racz, thank you for being a constant source of support.

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Tiffany R. Heline

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FIELD EVALUATION OF SOLVENT-FREE SAMPLING WITH DI-*N*-BUTYLAMINE FOR THE DETERMINATION OF AIRBORNE MONOMERIC AND OLIGOMERIC 1,6-HEXAMETHYLENE DIISOCYANATE

I. INTRODUCTION

1.1 GENERAL ISSUE

In the United States Air Force (USAF), preventing metal corrosion and surface deterioration on aircraft is essential to the flying mission. Corrosion prevention is accomplished using a variety of organic coatings including isocyanate-based polyurethane topcoats (AFCPCO, 2013). Isocyanates are typically one of the most hazardous chemical-based exposures at a USAF installation, thus warranting extensive air sampling by AF Medical Service personnel. Isocyanates are highly reactive, low-molecular weight chemicals containing one or more –N=C=O functional groups attached to an aromatic or aliphatic molecule. Isocyanates are classified, based on the number of N=C=O groups in the molecule, into diisocyanate monomers (two NCO groups) or polyisocyanates (three or more NCO groups) (Deft, 2011). Oligomers are a special class of low molecular weight polyisocyanates with 10 or fewer NCO groups. Polyurethane-based paints and coatings containing monomeric and oligomeric isocyanates are frequently selected as aircraft top coating because of their durability, flexibility, weatherability and abrasion, chemical and impact resistance (England and others, 2000a; England and others, 2000b). The most widely used isocyanates in US AF corrosion control operations are monomeric and oligomeric 1,6-hexamethylene diisocyanate (HDI) (EESOH-MIS, 2012).

Isocyanate exposure can cause contact dermatitis, asthma, and hypersensitivity pneumonitis; the most common adverse health outcome associated with isocyanate exposure is occupational asthma due to sensitization (Abadin and Spoo, 1998). Assessing and controlling employee exposure is important to minimize these adverse effects. Isocyanates have been a known hazard for decades with well documented sampling methods; however, the literature indicates the measurement of airborne isocyanate-containing compounds continues to be a challenge in the industrial hygiene field.

Selection of the most appropriate sampling and analytical method for quantitative monitoring of isocyanate exposure in a specific workplace environment is difficult for the following reasons: (1) isocyanates may be in the form of vapors or aerosols with various particle sizes; (2) the species of interest are reactive and unstable; (3) commercially available pure analytical standards are not available for all oligomeric isocyanates of interest and (4) low limits of detection are required. Some common sampling devices have included a variety of cassettes with treated filters, denuders, and impingers (Streicher and others, 1998; ISO, 2012).

There are several methods for the measurement and analysis of aerosol and vapor phase monomeric and oligomeric HDI including the National Institute for Occupational Safety and Health (NIOSH) Methods 5521, 5522, and 5525, as well as the ISO-CHEK® Sampler and the Occupational Safety and Health Administration (OSHA) Method 42. Numerous studies have been conducted comparing sampling results obtained using the methods listed above, each providing varying recommendations on individual method performance (England and others, 2000a; England and others, 2000b; Carlton and

England, 2000; Rudzinski and others, 2001; Rando and others, 2001; Thomasen and others, 2011; Ceballos and others, 2011; Reeb-Whitaker and others, 2012). There is no definitive sampling method best suited for all isocyanate sampling operations as, arguably, each method has limitations.

The current method preferred by the US Air Force School of Aerospace Medicine (USAFSAM) for sampling isocyanates is ASTM D6561 and D6562, commercially known as ISO-CHEK®. ISO-CHEK® was selected as the primary sampling method in the Air Force due to its ability to sample both monomeric and oligomeric HDI in the vapor and aerosol phase on a cassette. ISO-CHEK® consists of a two-stage filter arrangement that results in the separation of vapor from aerosol. Stage one contains an untreated Teflon filter to collect the aerosol phase, and stage two holds a glass fiber filter (GFF) impregnated with 9-(N-methylaminomethyl) anthracene (MAMA) designed to capture and derivatize the vapor phase isocyanates. Derivatization of the aerosol is accomplished by immediately placing the Teflon filter into 1-(2-methoxyphenyl) piperazine (MOPIP) in toluene solution after sampling (Omega Specialty Co, 2006; Batten, 2012).

1.2 PROBLEM STATEMENT

Several issues have been identified with the ISO-CHEK® sampling protocol: 1) the ISO-CHEK® protocol requires derivatization in the field, increasing the potential for sampling induced error, contamination, and under estimation if not immediately derivatized; 2) the ISO-CHEK® sampling media must be changed every 15 minutes, leading to increased disruptions and lost productivity while outfitting the industrial worker; 3) the sampling media requires stringent storage temperatures; 4) the media is relatively unstable with analysis recommended within 7 to 10 days; and 5) the derivatization solution is considered a hazardous material during shipment subject to Department of Transportation (DOT) hazmat compliance regulations. These combined issues indicate a need for further research and consideration of emerging isocyanate sampling technologies.

In response to these issues, a recent proposed alternative involves the use of di-*n*-butylamine (DBA) derivatization agent, used in conjunction with a combined denuder and filter sampler. This sampling technology is commercially available as the Supelco ASSET™ EZ4-NCO Sampler. In prior studies, fast reaction rates and stability towards interfering compounds were reported for the DBA reagent. DBA derivatives in combination with liquid chromatography (LC) and mass spectrometric (MS) detection have been demonstrated as a tool in the identification and quantification of isocyanates in air (Karlsson and others, 1998; Marand and others, 2005; Karlsson and others, 2005).

1.3 RESEARCH QUESTIONS

The objective of this research was to compare the current ISO-CHEK® sampling protocol utilized by the USAF, with the new commercially available Supelco ASSET™ EZ4-NCO Dry Sampler. The specific goal of this research was to compare the two sampling protocols and their ability to monitor employee exposures to monomeric and oligomeric HDI during aircraft polyurethane coating operations. This research will answer the following questions:

(1) Can adducts of 1,6-HDI as a dibutylamine derivative be quantified using liquid chromatography and mass spectrometric detection?

(2) Do the ISO-CHEK® and ASSET™ EZ4-NCO Dry Samplers collect an equivalent airborne HDI monomer concentration?

(3) Do the ISO-CHEK® and ASSET™ EZ4-NCO Dry Samplers collect an equivalent airborne HDI oligomer concentration?

(4) What is the relative cost of using the ASSET™ Sampler verse ISO-CHEK® for employee monitoring in the US Air Force?

1.4 SCOPE AND APPROACH

Side-by-side HDI air sampling was conducted at Stewart Air National Guard Base, Newburgh, NY during polyurethane spray finishing operations as part of a C-5M interior aircraft refurbishment to determine if there was a statistically significant difference between ISO-CHEK® and ASSET™ samplers. Two painters were sampled on 3 separate days during paint mixing, spraying, and gun cleaning processes using 15-minute partial period consecutive samples. ISO-CHEK® and ASSET™ samplers were clipped to the shoulder of the painters within the breathing zone. A total of 32 paired ISO-CHEK® and ASSET™ samples were collected using appropriate sampling trains and low-flow pumps. Descriptive statistics were gathered for each sampler including range, standard deviation, and mean. Paired *t*-tests (α-level of 0.05) were used to determine if the variability among ISO-CHEK® and ASSET™ samplers was significantly different.

1.5 SIGNIFICANCE

The focus of this thesis is to test the research hypothesis that a significant difference exists between the ISO-CHEK® and ASSET™ methods. If the ASSET™ sampler provides quantifiable results which are equally as sensitive, or more sensitive, for

HDI monomers and oligomers than the currently used ISO-CHEK® sampler it may provide a better field solution for industrial hygiene personnel to help ensure compliance and protection of worker health while using isocyanate-based corrosion control materials.

1.6 PREVIEW

This thesis was written in the scholarly article format with the intent for submission to the *Journal of Occupational and Environmental Hygiene*. The article is presented as Chapter II of this thesis, reformatted to maintain consistency within this document. The article primarily addresses the detection and quantification of HDI-DBA adducts as well as the ASSET™ and ISO-CHEK® relative collection efficiencies (Thesis Questions 1-3). Chapter III concludes the thesis by addressing Thesis Question 4 while readdressing the other 3 thesis questions. Appendices provide expanded material, such as an expanded literature review and detailed sampling results.

II. SCHOLARLY ARTICLE

Written for consideration of submission to the
Journal of Occupational and Environmental Hygiene
(http://www.oeh.tandfonline.com)

FIELD EVALUATION OF SOLVENT-FREE SAMPLING WITH DI-*N*-BUTYLAMINE FOR THE DETERMINATION OF AIRBORNE MONOMERIC AND OLIGOMERIC 1,6-HEXAMETHYLENE DIISOCYANATE

2.1 ABSTRACT

The purpose of this study was to perform a field evaluation of a new solvent-free (dry) sampling method using di-*n*-butylamine for the determination of airborne monomeric and oligomeric 1,6-hexamethylene diisocyanate (HDI). During the study, the new Sigma-Aldrich Supelco ASSET™ EZ4-NCO Dry Sampler was compared to the Omega Specialty Instrument Co. ISO-CHEK® sampler. Side-by-side HDI air sampling was conducted at an Air National Guard Base in New York, during polyurethane spray finishing operations as part of cargo aircraft refurbishment to determine if there was a statistically significant difference between ISO-CHEK® and ASSET™ samplers. Two painters were sampled on 3 separate days during paint mixing, spraying, and gun cleaning processes using 15-minute partial period consecutive samples.

A total of 32 paired ISO-CHEK® and ASSET™ samples were collected. Paired *t*-tests (α-level of 0.05) were used to determine if the variability among ISO-CHEK® and ASSET™ samplers was significantly different. This study suggests that the ASSET™ sampler collected significantly higher levels of HDI monomers ($P = 0.002$) indicating ISO-CHEK® may potentially underestimate employee's true exposures.

Nineteen of the 32 matched pairs were above the calibration range for HDI oligomers and were diluted in accordance with the Supelco method. The high degree of variability in HDI oligomer internal standard response indicated the 19 samples were biased during dilution. Paired *t*-tests (α-level of 0.05) conducted using all 32 matched pairs including the 19 diluted samples indicate the ASSET™ sampler collected significantly higher levels of HDI oligomer (*P*= 0.0358). When the matched-pairs are reduced to only those ASSET™ samples that were not diluted (*n* = 13), the paired *t*-test results indicate there is no significant difference in the collection efficiency of the ASSET™ and ISO-CHEK® samplers for HDI oligomers (*P* = 0.0772). Additional research using higher concentration calibration standards, once they are commercially available, is recommended to confirm the relationship between the ASSET™ and ISO-CHEK® HDI oligomer collection efficiencies.

2.2 INTRODUCTION

In the United States Air Force (USAF), preventing metal corrosion and surface deterioration on aircraft is essential to the flying mission. Corrosion prevention is accomplished using a variety of organic coatings including polyurethane topcoats that are capable of producing hazardous levels of airborne isocyanates during application. The hazardous polyurethane-based coatings are frequently selected because of their superior toughness, outdoor durability, and high chemical resistance (AFCPCO, 2013). The polyurethanes are a two component system: a base component containing polyols, pigments, solvents, and additives and a catalyst component containing solvents and 1,6-

hexamethylene diisocyanate (HDI) monomer and oligomers (AFCPCO, 2013; Deft, 2011).

Corrosion control personnel are potentially exposed to the overspray mist containing a mixture of reacted, partially reacted, and unreacted oligomers (Fent and others, 2006). The health hazards of HDI are well documented and include irritation of the mucous membranes of the eyes, nose and throat, and gastrointestinal and respiratory tracts. Irritation may be severe enough to produce bronchitis and bronchospasm. Sensitization and asthma are the primary health concerns with prevalence rates of 1 to 20 percent in the exposed workforce (Abadin and Spoo, 1998; Bello and others, 2004).

Isocyanates may be present in both the aerosol and vapor phase and, therefore, air sampling mechanisms should be capable of effectively capturing both phases. Many sampling mechanisms have been presented including impingers, impinger-filter combinations, sorbent tubes, denuder-filter combinations, and diffusive samplers (ISO, 2012). However, there is little agreement in the industrial hygiene field regarding the best sampling and analysis method for determining employee exposures to airborne isocyanates.

Further, isocyanates are highly reactive and unstable. Samples must be efficiently derivatized to stabilize the isocyanate and prevent reactions from occurring with polyols or water. Several reagents have been proposed to stabilize the reactive diisocyanates including 1-(9-anthracenylmethyl) piperazine (MAP), 1-(2-methoxyphenyl)piperazine (MOPIP), 1-(2-pyridyl)piperazine (1-2PP), 1,8-Diaminonaphthalene (DAN), di-*n*-butylamine (DBA), and 9-(N-methylamiomethyl) anthracene (MAMA). In addition to compound stability, there is also a lack of commercially available pure analytical standards as most standards are limited to derivatized monomers. Lastly, low occupational exposure limits drive the need for extremely sensitive analytical methods. Current analytical methods rely on high-performance liquid chromatography (HPLC) coupled with ultra-violet (UV), fluorescence (FL), or mass spectrometry (MS) detection (Bello and others, 2004; ISO, 2012; Streicher and others, 2000). Refer to

Table 1 for a list of published methods available for analyzing HDI monomers and oligomers. Further discussion on these methods can be found elsewhere in the literature (England and others, 2000a; England and others, 2000b; OSHA, 1989; NIOSH, 1994; NIOSH, 1998; NIOSH 2003).

Table 1. Standard Methods for Determining HDI Concentrations in Air

	ASSET™	**ISO-CHEK®**	**NIOSH 5521**	**NIOSH 5522**	**NIOSH 5525**	**OSHA 42**
Analyte	HDI Monomer HDI Polymers	HDI Monomer HDI Polymers	HDI Monomer HDI Polymers	HDI Monomer HDI Polymers	HDI Monomers HDI Polymers	HDI Monomer
Sampler	13-mm filter + denuder	37-mm closed-face double filter cassette	Impinger	Impinger	Filter, Impinger, or Impinger + Filter	37-mm single filter open-faced cassette
Sample Media	GFF + Denuder w/DBA	PTFE Filter field derivatized w/MOPIP, GFF w/MAMA	MOPIP in toluene	Tryptamine in DMSO	GFF w/MAP in 37-mm cassette or IOM sampler, or MAP in butyl benzoate	GFF w/1-2PP
Flow Rate (lpm)	0.2	1	1	1 – 2	1-2	1
Analysis	HPLC	HPLC	HPLC	HPLC	HPLC	HPLC
Detection	MS or MS/MS	UV/PDA	UV/PDA, EC	FL/EC	UV/FL	UV, FL
Standard Method Publication Year	2006 Monomer	2012 Monomer 2006 Polymer	1994	1998	2003	1989
Additional Comments	ISO 17734	ASTM 6561 ASTM 6562	Unrated NIOSH Evaluation	Partial NIOSH Evaluation, recommended for area sampling only	Partial NIOSH Evaluation	OSHA Evaluated Method

Notes: GFF = Glass Fiber Filter; DBA = di-*n*-butylamine; PTFE = polytetrafluoroehtylene; MOPIP = 1-(2-methoxyphenyl)piperazine; MAMA = 9-(N-methylamiomethyl)anthracene; DMSO = dimethyl sulfoxide; MAP = 1-(9-anthracenylmethyl)piperazine; IOM = Institute of Medicine; 1-2PP = 1-(2-pyridyl)piperzine; HPLC = High Performance Liquid Chromatography; MS = Mass Spectrometry; MS/MS = Tandem Mass Spectrometry; UV = ultraviolet; PDA = photodiode array; EC = electrochemical; FL = fluorescence .

In 2013, the Occupational Safety and Health Administration (OSHA) announced a new National Emphasis Program (NEP) aimed at reducing and eliminating the incidence of adverse health effects associated with occupational exposure to isocyanates. As part of the program, OSHA is requiring changes in how compliance officers conduct isocyanate sampling. Specifically, OSHA has recognized desorbing all filter samples in the field is a prudent practice. Therefore, OSHA has implemented a new standard operating procedure requiring compliance officers to perform field derivatization of all isocyanate filter samples. It is OSHA's position that immediate field derivatization stabilizes the highly reactive isocyanates and enhances recovery of the isocyanates that do not come into contact with the derivatization reagent coated on the filter (OSHA, 2013). OSHA's position is supported by prior research conducted by Schaeffer and others and Karoly (Schaeffer and others, 2013; Karoly, 1998).

In the US Air Force, airborne HDI monomer and oligomer exposures are currently sampled using the ISO-CHEK® sampler. ISO-CHEK® was selected as the primary sampling method in the Air Force due to its ability to sample both monomeric and oligomeric HDI in the vapor and aerosol phase on a single cassette (Batten, 2012). The sampling mechanism consists of a two-stage filter arrangement that results in the separation of vapor from aerosol. The first stage is an unimpregnated Teflon filter that collects isocyanate aerosols. After sampling, the Teflon filter is derivatized in the field using a MOPIP solution. The back filter is a MAMA-impregnated glass fiber filter that collects vapor phase isocyanates (ASTM D6561, 2011; ASTM D6562, 2012). Prior to the OSHA NEP, the second filter was derivatized in the laboratory. However, there are varying interpretations whether the new OSHA NEP recommendation for field desorption of all filters pertains to the ISO-CHEK® back filter. The Washington Division of Occupational Safety and Health (WA-DOSH) as well as Bureau Veritas North America (a commercial AIHA accredited laboratory) have interpreted this to mean the MAMA-impregnated back filter should be desorbed in the field. Alternatively, the USAFSAM laboratory (a Department of Defense AIHA accredited laboratory) continues to derivatize the back filter in the laboratory (OSHA, 2013; WA-DOSH, 2013).

In the literature, ISO-CHEK® performance has been compared to other methods including National Institute for Occupational Safety and Health (NIOSH) 5521, NIOSH 5522, Occupational Safety and Health Administration Method 42, and WA-DOSH samplers. Previous research efforts produced varied conclusions regarding the ISO-CHEK® HDI monomer performance. Thomasen and others reported ISO-CHEK® underestimated HDI monomer concentrations compared to a midget impinger containing MOPIP in solution. England and others (2000a & 2000b) concluded the ISO-CHEK® monomer concentration did not differ significantly from four other commonly used sampling methods (NIOSH 5521, NIOSH 5522, proposed NIOSH method, and OSHA 42). Thomasen and England also reported varied HDI oligomer results. Thomasen and others found ISO-CHEK® measured more HDI oligomers than the midget impinger containing MOPIP in solution; however, England once again found no significant difference between ISO-CHEK® and the NIOSH methods (Thomasen and others, 2011; England and others, 2000a; England and others, 2000b).

In addition to potentially underestimating HDI monomer concentrations, several issues have been identified with the ISO-CHEK® protocol: 1) filters require field derivatization; 2) rapid analysis is recommended (7 to 10 days after sampling); 3) media (cassette) swapout every 15 minutes may be disruptive to industrial operations; 4) sample storage at 4° C is recommended; and 5) MOPIP solution is considered a hazardous material subject to Department of Transportation (DOT) hazmat compliance regulations (Omega, 2006). Lastly, as of 2013, piperazine and related compounds including MOPIP were declared controlled substances in the United Kingdom. The UK Health and Safety Executive are liaising with the Home Office to acquire a license; until the license is received the use of MOPIP is effectively banned in the UK (Johnson, 2013).

The ASSET™ sampling mechanism consists of a two-stage denuder and filter arrangement. The first stage, the denuder, is a polypropylene tube coated with a di-*n*-butylamine (DBA)-impregnated GFF designed to capture vapor phase isocyanates. The second stage is a DBA-impregnated glass fiber filter that collects aerosol phase isocyanates (ISO, 2006E). In prior studies, fast reaction rates and stability towards interfering compounds were reported for the DBA reagent. DBA derivatives combined with HPLC-MS have been demonstrated as a tool in the identification and quantification of isocyanates in air (Karlsson and others, 1998; Marand and others, 2005; Karlsson and others, 2005).

Historically, ASSET™ sampling has been limited to isocyanate monomers due to the lack of available pure oligomer analytical standards. However, the manufacturer of the ASSET™ sampler recently released a certified reference material (ISO Guide 34:2009 and ISO/IEC 17025:2005) for HDI oligomers. Per the manufacturer, a single ASSET™ sampler may be used for over 8 hours which leads to increased productivity of the industrial worker and the potential for reduced analytical costs. Additionally, the

ASSET™ sampler is not derivatized in the field, nor does it have special DOT shipping requirements (Sigma-Aldrich, 2013).

The objective of this study was to compare the ISO-CHEK® method, currently used by the USAF, with the newer ASSET™ EZ4 NCO sampler technology during application of HDI-based polyurethane coatings using High Volume Low Pressure (HVLP) spray guns. Side-by-side HDI air sampling was conducted at an Air National Guard base during polyurethane spray finishing operations as part of cargo aircraft interior refurbishment, to determine if there was a statistically significant difference between ISO-CHEK® and ASSET™ samplers.

2.3 METHODS

Side-by-side HDI air sampling using low flow personal pumps was conducted during cargo aircraft interior refurbishment. A total of 32 HDI paired samples were collected. Two painters were sampled on 3 separate days during paint mixing, spraying, and gun cleaning processes using 15-minute partial period consecutive samples. ISO-CHEK® and ASSET™ samplers were placed within the breathing zone of the painters.

2.3.1 Painting Process

The paint used during this study was a two-part polyurethane gloss white paint manufactured by Deft Corporation, with Safety Data Sheets (SDS) listing 30 to 60 percent polymeric hexamethylene diisocyanate in the hardener (Deft Inc., 2011). While not listed on the SDS, the base may contain up to 1 percent HDI monomer. The coatings were mixed in a 3:1 base to hardener ratio (AFCPCO, 2013). No induction or dwell time was required before applying the coating and no cure accelerators were used. Polyurethane coatings were applied using HVLP spray guns to chine coves (voids adjacent to the floor in the cargo bay) as well as the flight deck hatches, galleys, and latrines. Painting was accomplished over 3 shifts, ranging from 89 to 172 minutes of actual paint application. Two portable air handlers were used to generate air movement from inside the aircraft into the hangar. The air handlers were fitted with filters to reduce the amount of overspray exiting the aircraft. All workers wore appropriate personal protection equipment including respiratory protection.

2.3.2 ISO-CHEK® Samplers

Sample Collection

ISO-CHEK® air samples were collected according to the manufacturer's recommendations using a SKC AirChek 2000 air sampling pump calibrated to a flow rate of 1 L min^{-1}, with a dual-stage 37 mm polystyrene cassette and a 5 µm PTFE membrane to trap the aerosol phase and a GFF impregnated with MAMA for the vapor phase(SKC 225-9023A). Sampling media was changed at 15 minute intervals. If the spray painting operation was completed in less time, then the cassette was removed on completion and actual collection time was documented. The PTFE filters were removed from the cassette with forceps and placed into a glass vial containing the MOPIP in toluene (0.1 mg ml^{-1}) desorbing solution. The vial was gently agitated to ensure the filter was saturated with the desorbing solution. The cassette containing the GFF was recapped and wrapped in foil to prevent UV degradation. The cassettes and the vials containing the PTFE filters were sealed and stored in a cooler (~4° C) and delivered to the USAFSAM Industrial Hygiene laboratory (an AIHA-accredited laboratory) for analysis.

HPLC-(PDA) UV Analysis

The USAFSAM Laboratory followed SOP 48-1184, *Analysis of Isocyanates by HPLC Using the ISO-CHEK® Method* in accordance with ASTM 6561-06 for aerosols and ASTM 6562-12 for vapors. Both the PTFE filters and the GFFs were analyzed using HPLC with photodiode array (PDA) detector UV for HDI monomer and oligomers. Readers are referred to the ASTM Standard Methods for additional details regarding the analysis procedures. All ISO-CHEK® samples were extracted within 10 days of collection in accordance with the manufacturer's recommendations.

The ISO-CHEK® method does not identify the types of isocyanates present based on specific oligomer standards. Instead, HDI oligomers are identified by comparing a diode array scan of the associated monomer standard with a diode array scan of the samples to identify the presence of oligomer peaks. Once identified, the areas of these peaks are summed and quantified using the response factor of the monomer peak and the concentration calculated using the molecular weight of an NCO equivalent (42 g/mol) (USAFSAM, 2013).

2.3.3 ASSET™ Samplers

Sample Collection

ASSET™ air samples were also collected according to the manufacturer's recommendations using a denuder and GFF impregnated with DBA (Supelco 5028-U).

The samplers were connected to a SKC AirChek 2000 air sampling pump pre-calibrated to a flow rate of 0.2 L min^{-1} using a low-flow adapter. The media was positioned in the breathing zone, near the ISO-CHEK® cassette. The ASSET™ media was changed every 15 minutes to mirror the ISO-CHEK® protocol. After sampling, the ASSET™ sampler was recapped and stored at room temperature (~25°C) until delivered to the Air Force Institute of Technology (AFIT) Environmental Laboratory for analysis.

Extraction

The AFIT Laboratory followed Supelco Method Rev 1.5, *Extraction and Analysis of ASSET™ EZ4-NCO Sampler* adapted from ISO 17734-1. The filter media from both the cassette and denuder were extracted with 3 ml of 1 mM H_2SO_4 (aq), 3 ml of methanol, and 5.5 ml of toluene in a 4 step procedure including shaking, sonicating, re-shaking, and centrifuging. After the samples were centrifuged, the top toluene layer was removed and placed in a new test tube. An additional 5.5 ml of toluene was added to the original sample and the extraction was repeated. The second toluene layer was added to the previous organic layer and evaporated to dryness using a nitrogen evaporator. Samples were re-dissolved in 1 ml of acetonitrile prior to analysis (Supelco Analytical, 2013).

HPLC-MS Analysis

For analysis of HDI-isocyanate derivatives, an Agilent Technologies 6130 single quadrupole HPLC-MS (Agilent Technologies, Santa Clara, CA) was used in the electrospray mode. The capillary voltage was 3.0 kV and the drying gas temperature was

260 °C. Selected ion monitoring was performed by monitoring positive ions (ESP$^+$ m/z = MH$^+$). Standard solutions including isocyanate-DBA and d$_9$-DBA derivatives of HDI monomer, biuret, dibiuret, tribiuret, isocyanurate, diisocyanurate, and triisocyanurate were obtained from the Institutet For Kemisk Analys (IFKAN, Norden AB, Sweden). Concentrations of the individual components in the chemical standards were determined by IFKAN using chemoluminscence nitrogen detection (LC-CLND), using caffeine as an external standard. The individual components in the standard solutions were characterized using LC-CLND and LC-MS.

The mass spectrometer was connected to a micro-LC pump. On-column focusing was performed using partially filled loops of 4+4 µl of 50/20/30 water/methanol/ acetonitrile. The DBA-isocyanate derivatives were analyzed using gradient elution for 18 minutes with a mobile phase of acetonitrile-water containing 0.005 percent formic acid. The LC column was an Ascentis Express C18 (5cm x 2.1mm, 2.7 µm particles). For identification, retention times of the sample peaks were compared to the standards and the internal standards. Quantification was accomplished by comparing the area ratio of the sample peak and the internal standard to the calibration plot. A “0-sample” was prepared by spiking a matrix solution with 100 µl of internal standard then extracting and re-dissolving the sample in 1 ml acetonitrile in an identical manner as the field samples. Concentrations outside the calibration range were diluted using the “0-sample” in accordance with the Supelco method. The analytical parameters for the HPLC-MS are summarized in Table 2.

Table 2. HPLC-MS Method Parameters

<table>
<tr><th colspan="2">HPLC</th><th colspan="2">MS</th></tr>
<tr><td>Column:</td><td>Ascentis Express
Length: 5 cm
Internal diameter: 2.1 mm
Particle diameter: 2.7 µm
Temperature: 40 °C</td><td>ESI:</td><td>Spray: 3.0 kV
Capillary temperature: 260 °C
Drying Gas Flow: 10 L/min
Nebulizer Pressure: 20 psi</td></tr>
<tr><td>Flow Rate:</td><td>0.4 ml min^{-1}</td><td>MS</td><td>Scan time: 0.48 s
Peak width: ±0.5 amu</td></tr>
<tr><td>Injection:</td><td>2 µL</td><td rowspan="3">SIM</td><td rowspan="3"><table>
<tr><th>Analyte</th><th>MW</th><th>SIM Mass</th></tr>
<tr><td>HDI-DBA</td><td>426.68</td><td>427.4</td></tr>
<tr><td>HDI-Biuret-DBA</td><td>865.7</td><td>866.8</td></tr>
<tr><td>HDI-Isocyanurate-DBA</td><td>892.3</td><td>892.8</td></tr>
<tr><td>HDI-d_9-DBA</td><td>444.68</td><td>445.4</td></tr>
<tr><td>HDI-Biuret-d_9-DBA</td><td>893.3</td><td>893.8</td></tr>
<tr><td>HDI-Isocyanurate-d_9-DBA</td><td>919.3</td><td>919.8</td></tr>
</table></td></tr>
<tr><td>Mobile Phase:</td><td>(A) 0.005% Formic Acid in 5:95 ACN: H_2O
(B) 0.005% Formic Acid in 95:5 ACN: H_2O</td></tr>
<tr><td>Gradient:</td><td><table>
<tr><th>Time</th><th>%A</th><th>%B</th></tr>
<tr><td>0</td><td>40</td><td>60</td></tr>
<tr><td>2</td><td>20</td><td>80</td></tr>
<tr><td>5</td><td>20</td><td>80</td></tr>
<tr><td>5.1</td><td>0</td><td>100</td></tr>
<tr><td>15.0</td><td>0</td><td>100</td></tr>
<tr><td>15.1</td><td>40</td><td>60</td></tr>
<tr><td>18</td><td>40</td><td>60</td></tr>
</table></td></tr>
</table>

2.4 RESULTS AND DISCUSSION

2.4.1 Chromatography

The single quadrupole HPLC-MS lacked the sensitivity required to resolve the internal standard peaks for the HDI-Dibiuret-d_9-DBA, HDI-Tribiuret-d_9-DBA, HDI-d_9-Diisocyanaurate-DBA, and HDI-Triisocyanurate-d_9-DBA. These compounds were removed from the selected ion monitoring (SIM) to increase the sensitivity for the remaining three compounds including HDI-DBA, HDI-Biuret-DBA, and HDI-Isocyanurate-DBA. Extracted chromatograms for HDI, biuret, and isocyanurate obtained during the analysis of an ASSET^{TM} field sample are shown in Figure 1.

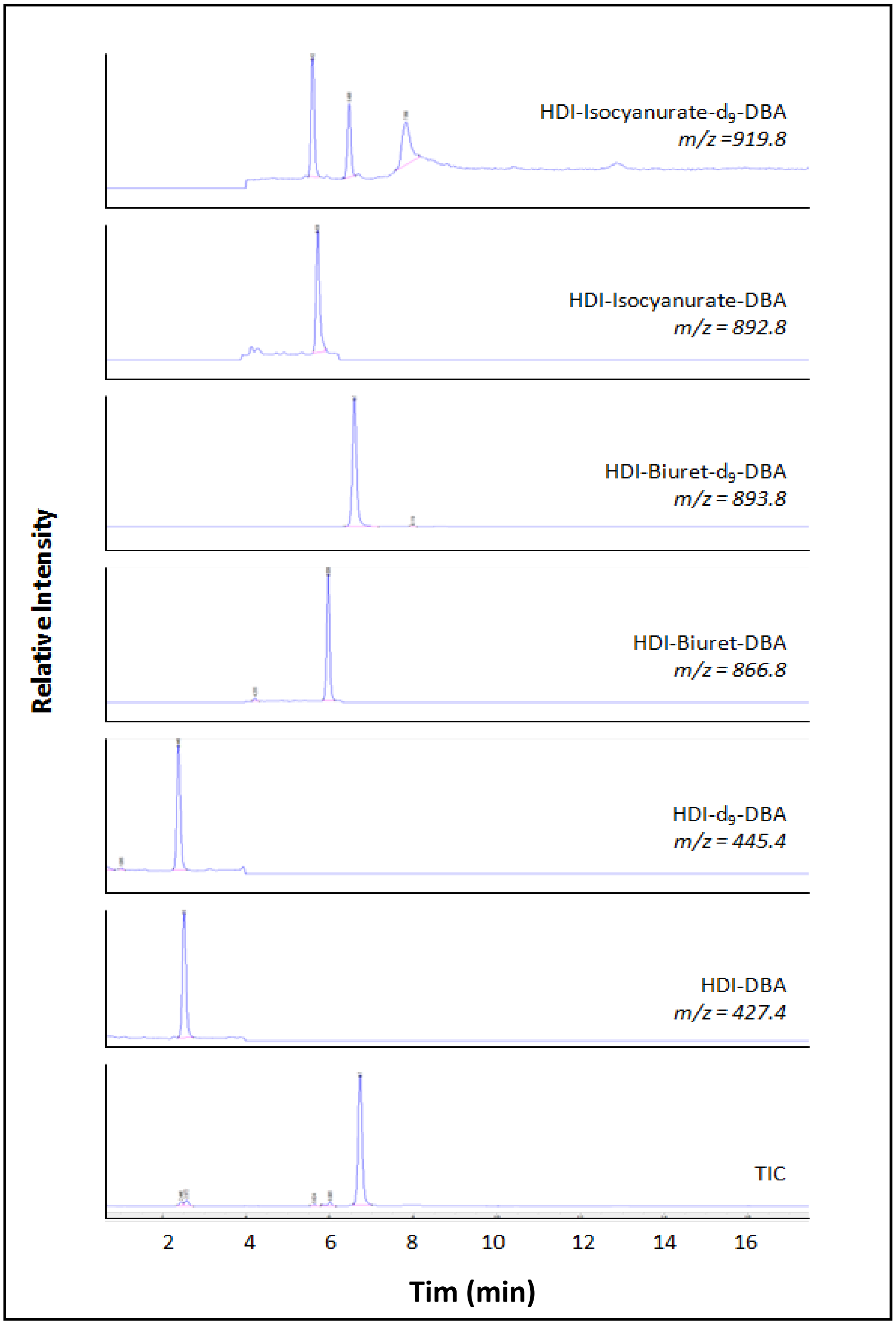


Figure 1. ASSET^{TM} Chromatogram, 5 cm Ascentis Express Column

Ion extractions using LC/MSD ChemStation (Agilent Technologies, Santa Clara, CA) were performed during data analysis to account for overlapping peaks. Following the ion extraction, sharp peaks were present in the resulting chromatograms with retention times between 2 and 8 minutes. Stereoisomers were present for HDI-Isocyanurate-d_9-DBA and quantification was based on the main peak. Isocyanurate was the dominant peak in the field samples.

2.4.2 Quantification and Recovery

In this study, the isocyanate-DBA derivatives were determined using HPLC-MS. Quantification was possible only for the HDI-DBA, HDI-Biuret-DBA, and HDI-Isocyanurate-DBA derivatives as the quadrupole HPLC-MS lacked the sensitivity required to resolve the internal standard peaks for the HDI-Dibiuret-DBA, HDI-Tribiuret-DBA, HDI-Diisocyanurate-DBA, and HDI-Triisocyanurate-DBA. The HDI Biuret and Isocyanurate concentrations were added together and reported as HDI Oligomers. One tenth, 1/100, and 1/1000 dilutions were required for isocyanurate. The analytical parameters are summarized in Table 3.

Table 3. HPLC-MS Quantification Data

Parameters	**HDI**	**Biuret**	**Isocyanurate**
Calibration Correlation Coefficient	0.999	0.9988	0.9995
Calibration Range (µg)	0.05-1.4	0.05-1.4	0.05-1.4
Relative Response Factor	1.0	0.39	0.15
CV ($n = 6$)	1.22	2.46	1.46
Recovery	99.4%	100.6%	83.1%

2.4.2 Statistics

A summary of the breathing zone concentrations measured by sampler type is provided in Table 4. The mean, range, and standard deviation are provided as measures of central tendency.

Table 4. Breathing Zone Concentrations for HDI Monomer and Oligomers

		HDI Monomer (mg/m^3)				HDI Oligomers (mg/m^3)			
Sampler	**N**	**Mean**	**Range**	**Std Dev**	**No.<LOQ**	**Mean**	**Range**	**Std Dev**	**No.<LOQ**
ASSET™	32	0.04759	0.0063-0.2670	0.06	13	8.03	0.01-76.54	15.7	7
ISO-CHEK®	32	0.01817	0.0065-0.0522	0.01	22	2.08	0.02-5.79	1.91	9

Refer to Figure 2 and Figure 3 for plots of the ASSET™ and ISO-CHEK® HDI monomer and oligomer matched pair concentrations. The plots indicate the variance in monomer and oligomer results is proportional to the measured concentration; the higher the measured air concentration, the greater the intersampler variance.

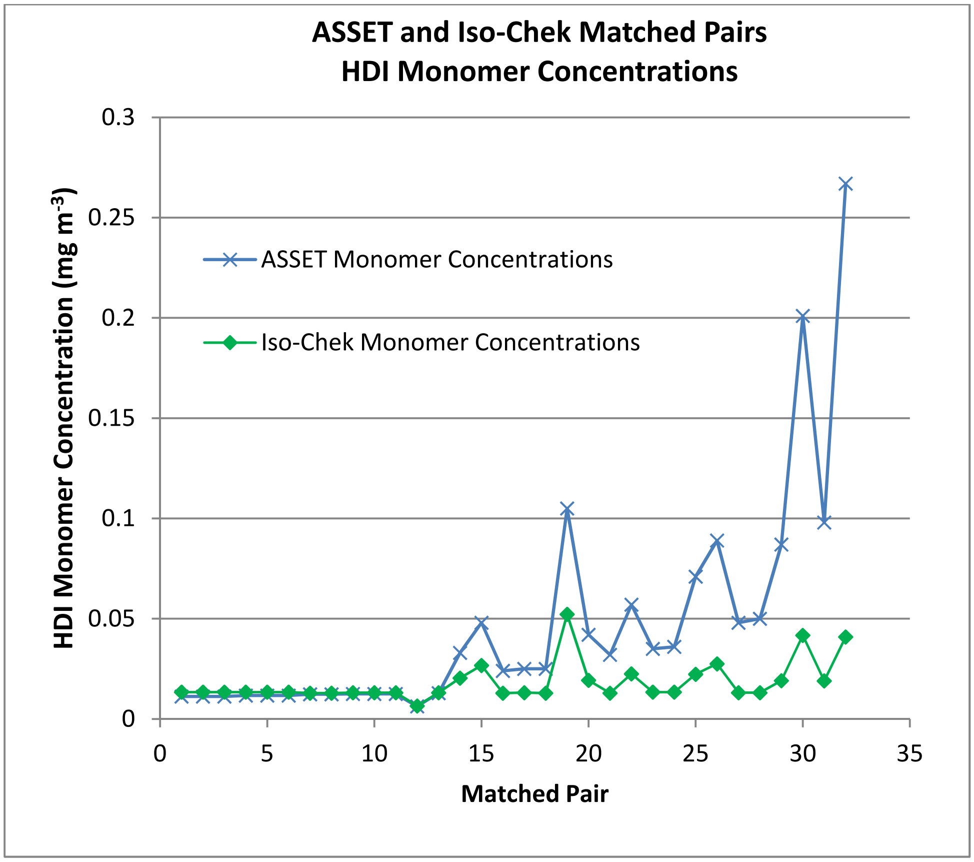


Figure 2. HDI Monomer Concentration Plot

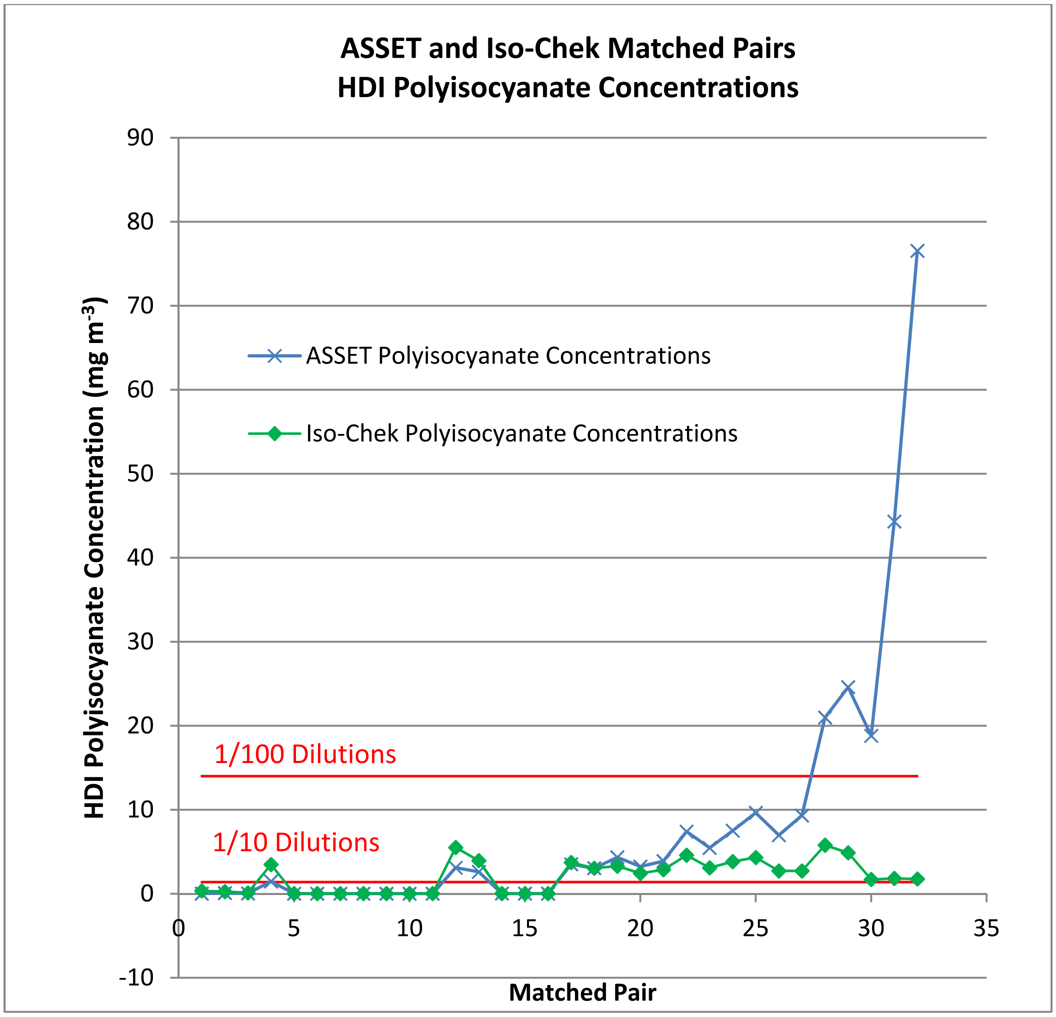


Figure 3. HDI Oligomer Concentration Plot

Paired *t*-tests (α=0.05) were conducted using JMP 9.0 (SAS Institute Inc., 2009) to explore whether significant differences existed between ASSET™ and ISO-CHEK® HDI monomer measurements. Measurements below the limit of quantification (LOQ) were calculated using the LOQ divided by the square root of 2. The ASSET™ sampler collected significantly higher levels of monomers (mean difference = 0.029 mg m^{-3}, P = 0.002). It should be noted, that 68% (22 out of 32) and 40% (13 out of 32) of ISO-CHEK® and ASSET™ samples, respectively, were below the LOQ for HDI monomer.

Paired *t*-tests (α=0.05) were also conducted to explore whether significant differences existed between ASSET™ and ISO-CHEK® HDI oligomer measurements. The ASSET™ sampler collected significantly higher levels of oligomers (mean difference = 5.95 mg m^{-3}, *P* = 0.0358). It should be noted that 19 of 32 ASSET™ samplers required dilution to fit on the calibration curve. The dilution protocol relies on a separately prepared and extracted sample containing only the internal standard. Recoveries of the internal standard were found to be highly variable [(Range 10,188-50,213 area counts), (Median: 21,117 area counts), (RSD: 51)]. Refer to Figure 4 for a box plot of the HDI-Isocyanurate-d9-DBA internal standard recovery variability. All samples were injected with 100 µl of the same internal standard solution prior to analysis. The dilution solution was prepared in a similar manner to the calibration samples. Based on Figure 4, the expected instrument response of the HDI-isocyanurate-d9-DBA internal standard in the dilution solution is approximately 40,000 area counts. However, the same 100 µl injection produces an instrument response as low as 10,000 area counts in the field samples. Because final isocyanate mass is determined based on the HDI-DBA to HDI-d9-DBA ratio, diluting a field sample having an internal standard area count of 10,000 with a dilution solution having an internal standard area count of 40,000 will bias results.

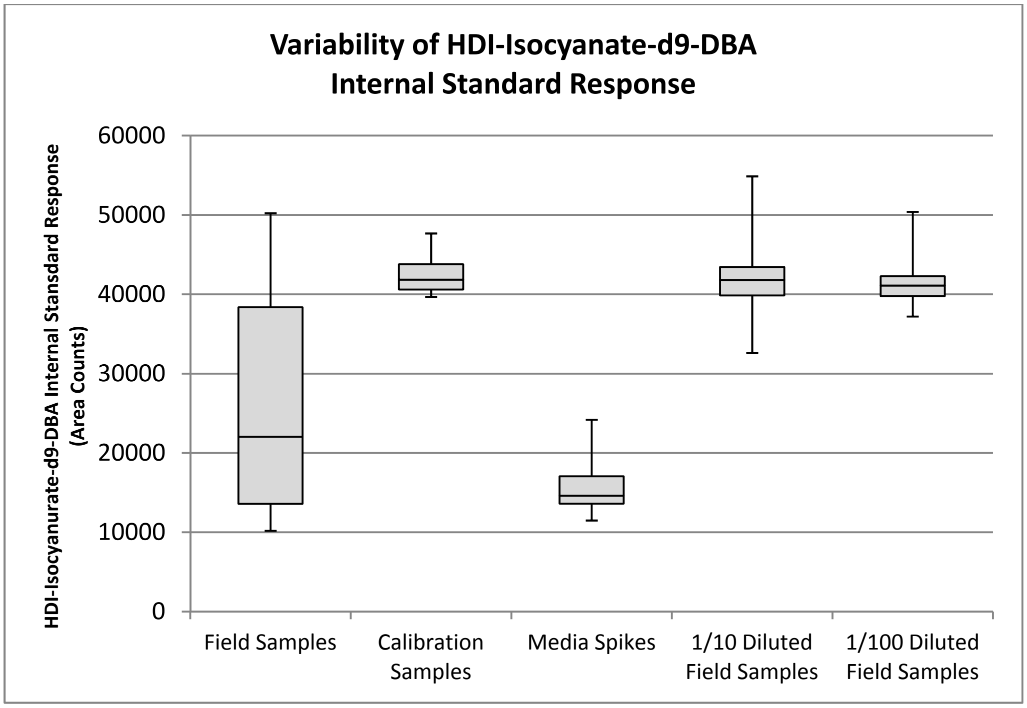


Figure 4. Variability of HDI-Isocyanurate-d9-DBA Internal Standard Response

The high variability in the internal standard response introduces bias into diluted sample results. This potential bias may account for some the intersampler variance noted for matched pairs above the 1/10 and 1/100 dilution lines in Figure 3. When the matched-pairs are reduced to only those ASSET^{TM} samples that were not diluted (n = 13), the paired *t*-test results indicate there is no significant difference in the collection efficiency of the ASSET^{TM} and ISO-CHEK$^{®}$ samplers for HDI oligomers (P = 0.0772).

2.7 CONCLUSIONS

The ASSET^{TM} sampler collected significantly higher levels of HDI monomers, indicating ISO-CHEK$^{®}$ samplers potentially underestimate true monomer exposures.

Because a high percent of the field samples required dilution, the variance in HDI oligomer concentrations was inconclusive. Additional research using higher concentration calibration standards, once they are commercially available, is recommended to confirm the relationship between the ASSET™ and ISO-CHEK® HDI oligomer collection efficiencies. Overall, the ASSET™ sampler presented as a user friendly option for industrial hygienists in the field worthy of additional research as a suitable alternative to the ISO-CHEK® samplers.

2.9 REFERENCES

The references used in this article are provided in the Reference section of the thesis, reformatted from that required by the *Journal of Occupational and Environmental Hygiene* to match the format adopted by this thesis.

III. CONCLUSIONS

3.1 CHAPTER OVERVIEW

This chapter concludes the thesis in its entirety, to include a review of the findings of Chapter II as well as conclusions drawn from the expanded literature review and expanded results and discussions presented in Appendices A and B, respectively.

3.2 REVIEW OF FINDINGS

3.2.1 Thesis Question 1: Analysis of HDI Oligomers by HPLC-MS

The identification and quantification of HDI oligomers by HPLC-MS was determined to be possible for a limited number of adducts, including biuret and isocyanurate. The internal standard for the higher molecular weight adducts including the di- and tri- compounds could not be resolved. Method parameters were varied to optimize instrument response during more than 200 HPLC-MS analytical runs totaling more than 150 hours of instrument run time.

Ascentis Express C18 Long Column

Initially, a longer Ascentis Express C18 column (15 cm x 4.6 mm, 2.7 µm) was used to increase the separation between the deuterated and undeuterated-DBA-isocyanate peaks. Instrument run times were extended up to 90 minutes to allow all compounds to elute; however, the HPLC-MS failed to resolve the HDI-triisocyanurate-DBA, HDI-triisocyanurate-d_9-DBA, and the HDI-tribiuret-d_9-DBA. Additionally, the HDI-biuret-

DBA and HDI-biuret- d_9-DBA peaks remained coeluted. Coelution was present for the triisocyanurate compounds as well.

During method development using the Ascentis Express long column, various adjustments were made to the method including: 1) flow rate; 2) column temperature; 3) injection volume; 4) gradient; 5) mobile phase; and 6) capillary temperature. The analytical parameters that resulted in the best separation and identification of oligomers using the 15 cm Ascentis Express Column are presented in Table 5. Other typical ion formations were also tried in addition to MH^+. Refer to Table 6 and Table 7 for a complete list of typical ion formations used in the SIM mode with the Ascentis Express long column. Refer to Figure 5 for the chromatogram produced using the analytical parameters in Table 5.

Table 5. HPLC-MS Method Parameters, 15 cm Ascentis Express Column

HPLC				MS		
Column:	Ascentis Express Length: 15 cm Internal diameter: 4.6 mm Particle diameter: 2.7 µm Temperature: 20 °C			ESI:	Spray: 3.0 kV Capillary temperature: 260 °C Drying Gas Flow: 10 L/min Nebulizer Pressure: 20 psi	
Flow Rate:	1.0 ml min^{-1}			SIM	Analyte	SIM Mass
					HDI-DBA	426.7
Injection:	2 µL				HDI-Biuret-DBA	866.3
					HDI-Isocyanurate-DBA	892.3
Mobile Phase:	(A) 0.01% Formic Acid in 5:95 ACN: H_2O				HDI-Dibiuret-DBA	1306.0
	(B) 0.01% Formic Acid in 95:5 ACN: H_2O				HDI-Diisocyanurate-DBA	1357.9
					HDI-Tribiuret-DBA	1614.6
					HDI-Triisocyanurate-DBA	1823.6
Gradient:	Time	%A	%B			
	0	60	40		HDI-d_9-DBA	444.7
	25.0	10	90		HDI-Biuret-d_9-DBA	893.5
					HDI-Isocyanurate-d_9-DBA	919.5
					HDI-Dibiuret- d_9-DBA	1342.2
					HDI-Diisocyanurate- d_9-DBA	1394.2
					HDI-Tribiuret- d_9-DBA	1788.9
					HDI-Triisocyanurate- d_9-DBA	1868.9

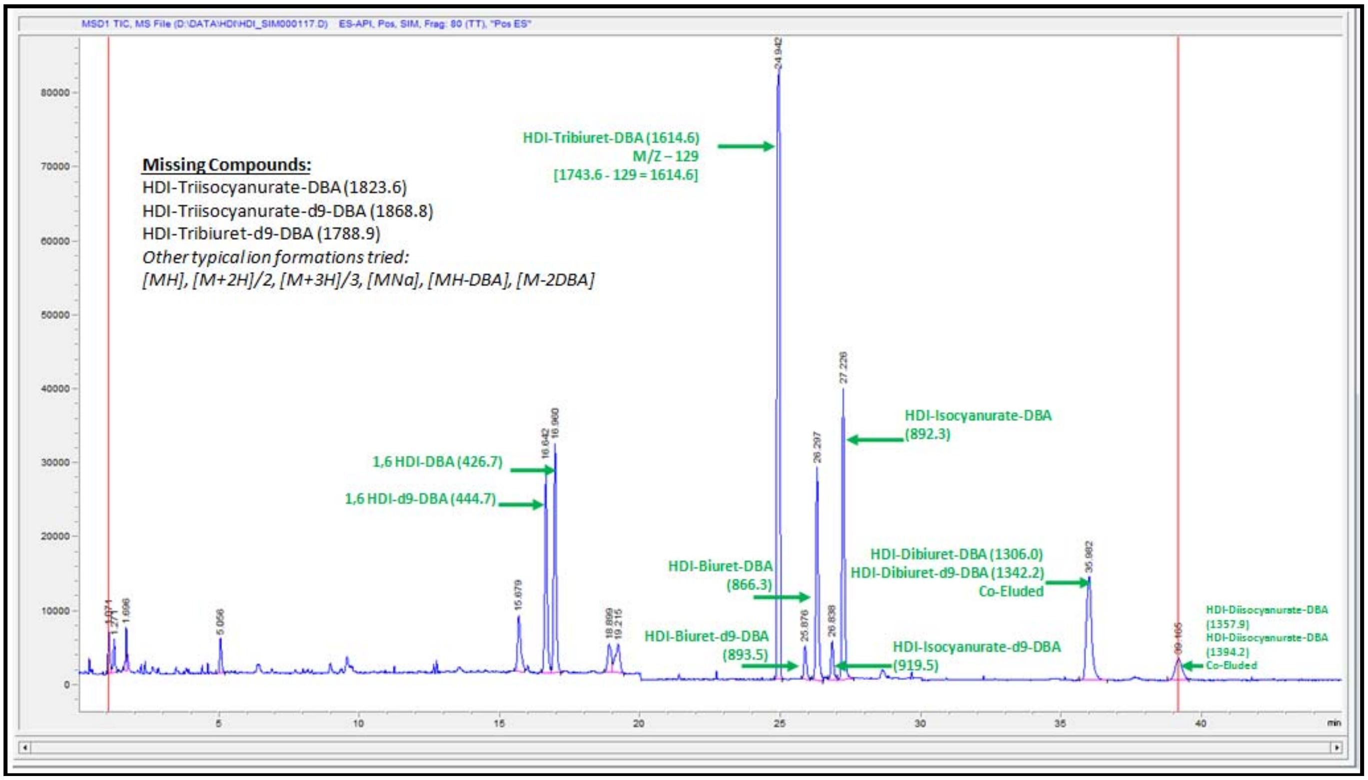


Figure 5. ASSET^{TM} Chromatogram, 15 cm Ascentis Express Column

ChemStation software was used to extract coeluting ions including dibiuret and diisocyanurate. However, when calibration curves were attempted using software ion extraction, the coefficient of determination (R^2) for dibiuret and diisocyanurate were suboptimum (<0.75). ISO 17734-1 stipulates an R^2 value of >0.98 as acceptable. Although the long column struggled to separate the higher molecular weight di- and tri-compounds, it did adequately identify and quantify HDI, biuret, and isocyanurate generating calibration curve R^2 values >0.99. Instrument analysis time for the long column was 45 minutes.

Table 6. Typical HDI-DBA Ion Formations

	Compound	Molar Mass (derivative g/mol)	*m/z*	Typical Ion Formation	
External Standards	1,6-HDI-DBA	426.7	427.5	[MH]$^+$	[M] + 1
			449.5	[MNa]$^+$	[M] + 23
			298.4	[MH-DBA]$^+$	[M] - 129
			130.2	[DBAH]$^+$	
			156.2	[DABCO]$^+$	
	HDI-Biuret-DBA	866.3	582	[MH]$^+$ - [$H_2NC_6H_{12}NHCONHC_6H_{12}NCO$]	[MH]+ - 284
			569	[MH]$^+$ - [NCOC6H12NCODBA]	[MH]+ - 297
			453	[MH]$_+$ - [DBANCO-CONC6H12NCODBA]	[MH]+ - 413
			440	[MH]$^+$ - [HDIDBA]	[MH]+ - 426
			414	[MH]+ - [H2NC6H12NHCONHC6H12N-CODBA]	[MH]+ - 452
			311	[MH]+ - [OCNC6H12NHCONHC6H12NCO]	[MH]+ - 555
			298	[MH]+ - [OCNC6H12NCODBAH]	[MH]+ - 568
			285	[MH]+ - [H2NC6H12NHCOCHC6H12NCO]	[MH]+ - 581
			272	[MH]+ - [H2NC6H12NCODBAH]	[MH]+ - 594
			143	[H2NC6H12NCOH]	
	HDI-Dibiuret-DBA	1306.0	1307	[MH]$^+$	[M] + 1
			1329	[MNa]$^+$	[M] + 23
			1177	[MH-DBA]$^+$	[M] - 129
			130.2	[DBAH]$^+$	
			156.2	[DABCO]$^+$	
			653.82	[M+2H]/2 (Doubly Charged)	
	HDI-Tribiuret-DBA	1743.6	1744.6	[MH]$^+$	[M] + 1
			1766.6	[MNa]$^+$	[M] + 23
			1614.6	[MH-DBA]$^+$	[M] - 129
			130.2	[DBAH]$^+$	
			156.2	[DABCO]$^+$	
			873.647	[M+2H]/2 (Doubly Charged)	
	HDI-Isocyanurate-DBA	892.3	893.3	[MH]$^+$	[M] + 1
			914.3	[MNa]$^+$	[M] + 23
			634	[MH]+ - 2DBA	[M] - 258
			608	[MH]+ - [H2NC6H12NHCONHC6H12NCO]	[M] - 284
			479	[MH]+ - [H2NC6H12NHCONHC6H12NCODBA]	[M] - 413
			763.3	[MH-DBA]$^+$	[M] - 129
	HDI-Diisocyanurate-DBA	1357.9	1358.9	[MH]$^+$	[M] + 1
			1380.9	[MNa]$^+$	[M] + 23
			1228.9	[MH-DBA]$^+$	[M] - 129
			130.2	[DBAH]$^+$	
			156.2	[DABCO]$^+$	
			680	[M+2H]/2 (Doubly Charged)	
	HDI-Triisocyanurate-DBA	1823.6	1824.6	[MH]$^+$	[M] + 1
			1846.6	[MNa]$^+$	[M] + 23
			1694.6	[MH-DBA]$^+$	[M] - 129
			130.2	[DBAH]$^+$	
			156.2	[DABCO]$^+$	
			912.626	[M+2H]/2 (Doubly Charged)	

Table 7. Typical HDI-d$_9$-DBA Ion Formations

	Compound	Molar Mass (derivative g/mol)	*m/z*	Typical Ion Formation	
Internal Standards	1,6-HDI-d9-DBA	444.7	445.7	[MH]$^+$	[M] + 1
			467.7	[MNa]$^+$	[M] + 23
			315.7	[MH-DBA]$^+$	[M] - 129
			130.2	[DBAH]$^+$	
			156.2	[DABCO]$^+$	
	HDI-Biuret-d9-DBA	893.5	894.5	[MH]$^+$	[M] + 1
			916.5	[MNa]$^+$	[M] + 23
			764.5	[MH-DBA]$^+$	[M] - 129
			130.2	[DBAH]$^+$	
			156.2	[DABCO]$^+$	
	HDI-Dibiuret-d9-DBA	1342.2	1343.2	[MH]$^+$	[M] + 1
			1365.2	[MNa]$^+$	[M] + 23
			1213.2	[MH-DBA]$^+$	[M] - 129
			672.0	[M+2H]/2 (Doubly Charged)	
			130.2	[DBAH]$^+$	
			156.2	[DABCO]$^+$	
	HDI-Tribiuret-d9-DBA	1788.9	1789.9	[MH]$^+$	[M] + 1
			1811.9	[MNa]$^+$	[M] + 23
			1659.9	[MH-DBA]$^+$	[M] - 129
			895.6	[M+2H]/2 (Doubly Charged)	
			130.2	[DBAH]$^+$	
			156.2	[DABCO]$^+$	
	HDI-Isocyanurate-d9-DBA	919.5	920.5	[MH]$^+$	[M] + 1
			942.5	[MNa]$^+$	[M] + 23
			790.5	[MH-DBA]$^+$	[M] - 129
			130.2	[DBAH]$^+$	
			156.2	[DABCO]$^+$	
	HDI-Diisocyanurate-d9-DBA	1394.2	1395.2	[MH]$^+$	[M] + 1
			1417.2	[MNa]$^+$	[M] + 23
			1265.2	[MH-DBA]$^+$	[M] - 129
			698.0	[M+2H]/2 (Doubly Charged)	
			130.2	[DBAH]$^+$	
			156.2	[DABCO]$^+$	
	HDI-Triisocyanurate-d9-DBA	1868.8	1869.8	[MH]$^+$	[M] + 1
			1891.8	[MNa]$^+$	[M] + 23
			1739.8	[MH-DBA]$^+$	[M] - 129
			935.6	[M+2H]/2 (Doubly Charged)	
			130.2	[DBAH]$^+$	
			156.2	[DABCO]$^+$	

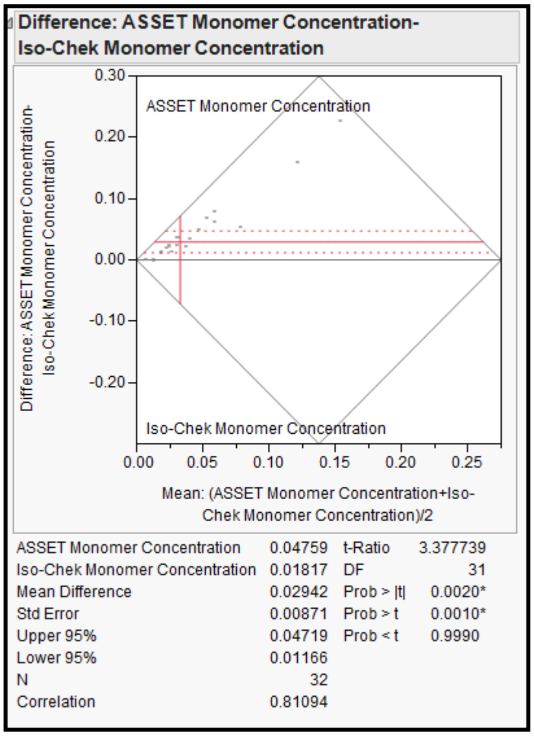
Ascentis Express C18 Short Column

Refer to Table 2 in Chapter II for the Ascentis Express 5 cm method parameters. Similar to the long column, the short column was unable to resolve the di- and tri- compounds. The short column method development procedures mirrored the long column procedures. Instrument parameters were adjusted to optimize HDI oligomer detection and quantification. It was concluded that the short column could adequately identify and quantify HDI, biuret, and isocyanurate in the range of 0.05 to 1.4 µg ml^{-1}, with all compounds having calibration curve R^2 values of 0.999, 0.9988, and 0.9995 respectively. One tenth, 1/100, and 1/1000 dilutions were required for HDI isocyanurate. Bias introduced by these dilutions is discussed in paragraph 3.3.5, but it should be emphasized here that quantification of HDI biuret and isocyanurate is limited to the calibration range tested. Instrument analysis time for the short column was 18 minutes.

3.2.2 Thesis Question 2: ASSET™ and ISO-CHEK® Monomer Collection Efficiency

Paired *t*-tests ($\alpha=0.05$) were conducted using JMP 9.0 (SAS Institute Inc., 2009) to explore whether significant differences existed between the ASSET™ and ISO-CHEK® monomer concentrations. Measurements below the limit of quantification (LOQ) were calculated using the LOQ divided by the square root of 2. The ASSET™ sampler collected significantly higher levels of monomers (mean difference = 0.029 mg m^{-3}, $P = 0.002$). It should be noted that 22 and 13 ISO-CHEK® and ASSET™ samplers respectively were below the LOQ for HDI monomer. The single full shift ASSET™ sample measured an 8 hr time-weighted average (TWA) monomer concentration of 0.0155 mg m^{-3} compared to the corresponding partial shift consecutive ISO-CHEK®

samples 8 hr TWA of 0.0072 mg m^{-3}. The percent difference in the two methods was 36.5. Refer to Figure 6 for the monomer paired *t*-test results produced in JMP.

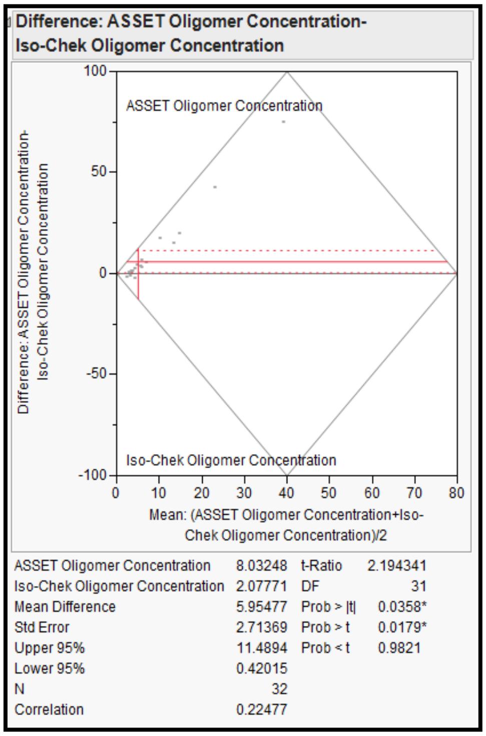


```
ASSET Monomer Concentration     0.04759  t-Ratio    3.377739
Iso-Chek Monomer Concentration  0.01817  DF               31
Mean Difference                 0.02942  Prob > |t|  0.0020*
Std Error                       0.00871  Prob > t    0.0010*
Upper 95%                       0.04719  Prob < t    0.9990
Lower 95%                       0.01166
N                                    32
Correlation                     0.81094
```

Figure 6. ASSET^{TM} and ISO-CHEK$^{®}$ Monomer Paired *t*-test

3.2.3 Thesis Question 3: ASSET^{TM} and ISO-CHEK$^{®}$ Oligomer Collection Efficiency

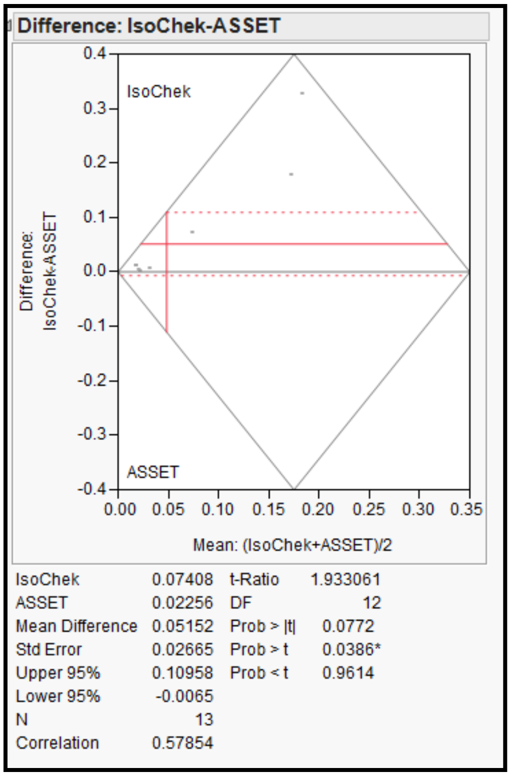
Paired *t*-tests (α=0.05) were also conducted to explore whether significant differences existed between the ASSET^{TM} and ISO-CHEK$^{®}$ oligomer concentrations. The ASSET^{TM} sampler collected significantly higher levels of oligomers (mean difference = 5.95 mg m^{-3}, *P* = 0.0358). Refer to Figure 7 for the paired *t*-test results produced in JMP. However, referring to paragraph 3.3.5, it should be noted that 19 of 32 ASSET^{TM} samplers required dilution to fit on the calibration curve. The dilutions are a significant source of bias that is not reflected in the paired *t*-test results. Additional research is required to determine the extent of the bias and the impact on the research findings.



```
ASSET Oligomer Concentration    8.03248  t-Ratio   2.194341
Iso-Chek Oligomer Concentration 2.07771  DF              31
Mean Difference                 5.95477  Prob > |t|  0.0358*
Std Error                       2.71369  Prob > t    0.0179*
Upper 95%                       11.4894  Prob < t    0.9821
Lower 95%                       0.42015
N                                    32
Correlation                     0.22477
```

Figure 7. ASSET™ and ISO-CHEK® HDI Oligomer Paired *t*-test (*n*=32)

When the matched-pairs are reduced to only those ASSET™ samples that were not diluted (*n* = 13), the paired *t*-test results indicate there is no significant difference in the collection efficiency of the ASSET™ and ISO-CHEK® samplers for HDI oligomers (*P* = 0.0772). Refer to Figure 8 for the paired *t*-test results produced in JMP.



```
IsoChek          0.07408  t-Ratio    1.933061
ASSET            0.02256  DF               12
Mean Difference  0.05152  Prob > |t|   0.0772
Std Error        0.02665  Prob > t     0.0386*
Upper 95%        0.10958  Prob < t     0.9614
Lower 95%        -0.0065
N                     13
Correlation      0.57854
```

Figure 8. ASSET^{TM} and ISO-CHEK$^{®}$ HDI Oligomer Paired *t*-test (*n*=13)

One possible conclusion is that there is truly no significant difference in the collection efficiencies. Alternatively, one could conclude there is no significant difference at lower concentrations but a significant difference may exist at higher concentrations. Additional testing is required to determine which hypothesis is correct.

3.2.4 Thesis Question 4: Cost Analysis

A rudimentary cost analysis was conducted to determine the fiscal feasibility of adopting the ASSET^{TM} method at the USAFSAM Industrial Hygiene laboratory in the future. To aid in the cost-benefit determination, a summary of the isocyanate analyses conducted by the USAFSAM/OEA laboratory was pulled from the laboratory information management system (LIMS). Summary statistics from the LIMS isocyanate data pull are provided in Table 8.

Table 8. Summary of Isocyanate Analyses Completed by USAFSAM/OEA, 2008-2013

Summary Statistic		**Percent of Total**
Total number of isocyanate samples analyzed	3748	
Unique work orders	313	
Average laboratory turnaround time	20 days	
Average number of samples per work order	12	
Samples analyzed by OSHA Method 42	41	1.1%
Samples analyzed by ISO-CHEK$^{®}$	3707	98.9%
Samples requesting isocyanates other than HDI	484	12.9%
Samples requesting HDI monomer	1663	44.4%
Samples requesting HDI Oligomers	1600	42.7%
Samples with ISO-CHEK$^{®}$ volumes > 30 liters	585	15.6%
Samples with ISO-CHEK$^{®}$ flow rates >1 l min^{-1}	0	0%
Samples below the laboratory reporting limit	2859	76.3%

A few conclusions can be drawn from the summary statistics: 1) the frequency of combined HDI monomer and oligomer analyses (87% of total isocyanate analyses) is consistent with the relative abundance of HDI in industrial workcenters (85%); 2) ISO-CHEK$^{®}$ is the predominant method used by AF Medical Service personnel; 3) nearly 16% of ISO-CHEK$^{®}$ samples may have been improperly collected as sample volumes were greater than the 30 liters recommended by the manufacturer; and 4) a more sensitive method with a lower laboratory reporting limit may aid in health risk assessments for 76% of the samples analyzed by the laboratory.

For the cost analysis, the following assumptions were made to aid in determining costs:

(1) The average ISO-CHEK® work order consists of 5 field samples and 1 field blank

(2) All 5 field samples are collected from 1 employee during a single shift

(3) The projected ASSET™ work order will consist of 1 full-shift field sample and 1 blank

(3) Sixty-two work orders are processed each year, or 1.2 per week

(4) Monomeric and oligomeric fractions are requested for each sample

(5) Laboratory chemical supplies are purchased in bulk, enough to last 1-5 years

If the ASSET™ sampling method was adopted by USAFSAM, there would likely be a corresponding increase in sampling frequency due to the relative ease of sample collection compared to ISO-CHEK®. However, this increase cannot be quantified and therefore is not included in the cost analysis. Additionally, no attempt was made to quantify laboratory man-hours. The ASSET™ method is in its infancy and inter-technician sample preparation time likely remains highly variable until the method is established. It should be noted that the double extraction required for the ASSET™ method is time intensive; this additional workload has not been captured in the cost analysis. Also the cost of nitrogen gas supply was not included as it was deemed negligible and equivalent for both methods. Lastly, no cost was associated with the Agilent 1200 Series HPLC-UV and Zorbax Eclipse XDB C18 column required for ISO-CHEK® analysis as these pieces of equipment were assumed to be in place and currently used for routine analyses.

Refer to Table 9 for the 1 and 5-year cost for continuing ISO-CHEK® sampling in the US Air Force. All prices were first obtained from government contract suppliers listed on the General Services Administration (GSA) Advantage website. Manufacturer's pricing was used when GSA pricing was not available.

Table 9. ISO-CHEK® Cost Analysis

1 and 5 Year ISO-CHEK® Cost Analysis						
Number of Samples Analyzed Per Year	372					
QC Samples (Cal Stds & Media Spikes)	148*	*Includes 2 media spikes/workorder and 4 calibration curves/yr				
Number of Samples Analyzed in Next 5 Years	1860					
Sample Collection	**Price**	**Unit**	**Price/Sample**	**Cost/Year**	**Cost/5 Yr**	**Source**
ISO-CHEK® Cassette	$231.00	10/pk	$23.10	$8,593	$42,966	SKC
Foil for cassettes	$8.30	500/shts	$0.02	$6	$31	SKC
Laboratory Chemicals	**Price**	**Unit**	**Required/Yr**	**Cost/Yr**	**Cost/5 Yr**	**Source**
Acetonitrile, HPLC grade	$95.91	4 L	5 L	$120	$599	GSA
Acetic acid, glacial, HPLC grade	$59.41	2.5 L	as needed	$12	$59	GSA
Acetic anhydride, ACS certified grade	$23.61	100 mL	5 mL	$5	$24	GSA
ASTM Type II Water, or better	$42.74	20 L	50 L	$107	$534	GSA
1,6-HDI Neat	$266.50	1 g	10 µl	$53	$267	SKC
Isocyanate-MAMA derivative solution in DMF	$64.95	1 g	5 ml	$13	$65	SKC
MOPIP, 98% chemical purity	$32.40	5 g	160 mg	$6	$32	Sigma-Aldrich
N,N-dimethylformamide, reagent grade	$54.23	500 mL	800 ml	$87	$434	GSA
Phosphoric acid, ACS reagent grade	$38.07	1 L	as needed	$8	$38	GSA
Sodium Acetate, ACS certified grade	$184.50	500 g	12.5 g	$5	$185	FisherSci
Triethylamine, 98% chemical purity	$81.95	1 L	1 L	$82	$410	GSA
Toluene, HPLC grade	$51.02	4 L	2 L	$26	$128	GSA
Laboratory Equipment	**Price**	**Unit**	**Required/Yr**	**Cost/Yr**	**Cost/5 Yr**	**Source**
0.45 µm PTFE syringe filter	$137.50	100/pk	768	$1,056	$5,280	GSA
2 ml amber glass autosampler vials	$12.95	100/pk	892	$116	$578	GSA
PTFE crimp top closures	$12.49	100/pk	892	$111	$557	GSA
Disposable plastic pipettes	$10.79	500/pk	892	$19	$96	GSA
Disposable plastic 5 ml syringes	$18.22	100/pk	892	$163	$813	GSA
Screw-cap 16 x 125 mm test tubes w/PTFE caps	$469.03	288/pk	520	$847	$4,234	GSA
Glass fiber filters, 37 mm, 1.0 µm	$78.75	100/pk	124	$98	$488	SKC
PTFE filter, 37 mm, 5.0 µm	$147.00	50/pk	124	$365	$1,823	SKC
Candle Jars	$88.01	43/pk	520	$1,064	$5,322	GSA
Total				***$12,960***	***$64,962***	

Equipment required for ASSET™ sample preparation and analysis was assumed to be owned by USAFSAM and included a nitrogen evaporator, shaker, ultrasonic bath, and centrifuge. The initial purchase of this equipment was not included in the cost analysis. The research in this thesis was based on the use of HPLC-MS since it was the instrument available in the AFIT laboratory; however, for costs comparisons the purchase price of an HPLC-MS/MS should be considered (~$240K, Agilent). Tandem MS has proven to provide better analytical results for isocyanates, and thus is assumed to be the preferred instrument for new purchase. An Ascentis Express 5 cm C18 column must be purchased as well ($585, Supelco). Refer to Table 10 for the 1 and 5-year cost for performing ASSET™ analysis in the USAFSAM/OEA analytical laboratory. All prices were first obtained from government contract suppliers listed on the General Services Administration (GSA) Advantage website. Manufacturer's pricing was used when GSA pricing was not available.

The yearly cost for ASSET™ analysis is $6.3 K compared to $13.0 K for ISO-CHEK® analysis, resulting in a 50 percent reduction in isocyanate analytical costs. Comparing the 5 year cost, ISO-CHEK® is $32K more expensive. Based on the cost savings, the ASSET™ sampler would recoup the cost of purchasing a new HPLC-MS/MS in 7.5 years.

Table 10. ASSET^{TM} Cost Analysis

ASSET^{TM} 1 and 5 Year Cost Analysis						
Number of Samples Analyzed Per Year	124					
Associated QC Samples ((Cal Stds & Media Spikes)	148*	*Includes 2 media spikes/workorder and 4 calibration curves/yr				
Number of Samples Analyzed in Next 5 Years	620					
Sample Collection	**Price**	**Unit**	**Price/Sample**	**Cost/Year**	**Cost/5 Yr**	**Source**
ASSET^{TM} Sampler	$427.50	10/pk	$42.75	$5,301	$26,505	Sigma-Aldrich
Laboratory Chemicals	**Price**	**Unit**	**Required/Yr**	**Cost/Yr**	**Cost/5 Yr**	**Source**
HDI-DBA Oligomer Standard	$60.00	1 mL	1 mL	$60	$300	Sigma-Aldrich
HDI-DBA-d9 Oligomer Standard	$60.00	1 mL	3 mL	$180	$900	Sigma-Aldrich
Dibutylamine	$39.04	500 mL	100 mL	$8	$39	GSA
Acetic Acid	$59.41	2.5 L	36 mL	$12	$59	GSA
Sulfuric Acid	$18.27	1 L	50 mL	$4	$18	GSA
Acetonitrile	$95.91	4 L	2 L	$48	$240	GSA
Methanol	$34.81	4 L	2 L	$17	$87	GSA
Toluene, HPLC grade	$51.02	4 L	3 L	$38	$191	GSA
Formic Acid	$61.93	100 mL	26 mL	$3	$16	GSA
HPLC Grade Water	$30.42	4 L	500 mL	$4	$19	GSA
Laboratory Equipment	**Price**	**Unit**	**Required/Yr**	**Cost/Yr**	**Cost/5 Yr**	**Source**
2 ml amber glass autosampler vials	$12.95	100/pk	272	$35	$176	GSA
PTFE crimp top closures	$12.49	100/pk	272	$34	$170	GSA
Pasteur Pipets	$55.00	1440/ea	272	$10	$52	GSA
Disposable plastic 5 ml syringes	$18.22	100/pk	272	$50	$248	GSA
15 mL Round bottom centrifuge tube w/cap and PTFE liners	$124.55	500/pk	272	$68	$339	GSA
Screw-cap 16 x 125 mm test tubes w/PTFE caps	$469.03	288/pk	272	$443	$2,215	GSA
Glass fiber filters, 37 mm, 1.0 µm	$78.75	100/pk	124	$98	$488	Sigma-Aldrich
Total				$6,315	$32,062	

3.3 LIMITATIONS

Several limitations were identified during the analysis of the ASSET^{TM} samplers with potential impact on the research findings. This study was limited to the application of two-part polyurethane gloss white paint manufactured by Deft Corporation using a HVLP spray gun. The field evaluation does not account for isocyanates other than HDI, HDI biuret, and HDI isocyanurate and is limited to the spray painting process sampled. A total of 43 HDI paired samples were collected. The initial study design included an additional aim to evaluate inter-laboratory variability of analytical results by sending 4 of the paired ASSET™ samples to a secondary laboratory; however, this aim was abandoned when an issue was identified during extraction at the second laboratory. There was an issue analyzing the internal standard for an additional 7 samples at the primary lab. Therefore, the total number of paired samples analyzed was 32. Additional details regarding the research limitations are discussed in the following paragraphs.

3.3.1 Inter-laboratory Validation

Samples sent to Bureau Veritas North America (BVNA) aimed at testing inter-laboratory variability were lost due to error during extraction. The analytical quality control samples associated with the field samples sent to BVNA yielded recoveries ranging from 4 to 83 percent. Recoveries were much lower than expected; historically recoveries ranged 80 to 95 percent.

Subsequent studies performed by BVNA concluded the low recoveries were most likely due to the length of time the samples were allowed to remain in the desorbing solvent prior to full extraction (in this case, 2 days). In BVNA's opinion, allowing the samples to remain in the acidic desorbing solvent changed the chemistry of the analytes in solution. Due to the low and inconsistent recoveries, all analytical results received from BVNA may only be viewed qualitatively. Six additional samples extracted by AFIT were sent to BVNA for analysis; analysis is still pending. A full inter-laboratory comparison to include extraction is not possible; however, once results are received for the second set of samples a limited comparison may be made.

3.3.2 HPLC-MS Sensitivity

The single quadrupole HPLC-MS used by AFIT was not sensitive enough to resolve the di- and tri- deuterated internal standard compounds. Oligomer quantification was based on 2 of the 6 oligomers available in the standard. A review of the BVNA qualitative results indicate the di- and tri- compounds may account for 13 to 37 percent of the total oligomer concentration. Thus, HDI oligomer measurements may be underestimated by as much as 37 percent using the ASSET™ method described in this research.

3.3.3 Sample Stability Testing

ASSET™ samples were extracted 62 days post sampling. No research has reported recoveries past 30 days. A study is currently underway at AFIT to test sample stability on the filter at 30, 60, and 90 days post collection. Results will not be available until March 2014.

3.3.4 Peak Separation

True peak separation was not achieved on the HPLC-MS. Coelution was witnessed for internal and external standards for all three compounds. Quantification was dependant on ChemStation software for ion extraction. It is hypothesized that the lack of HPLC-MS sensitivity may be due to instrument configuration, to include the length of tubing from the pump to the injection valve, from the injection valve to the column, and from the column to the MS.

3.3.5 *Dilutions*

The calibration range was limited due to the concentrations of available analytical standards. External and internal standards were prepared by IFKAN with functional concentrations of 10 µg ml^{-1} with respect to the DBA and DBA-d_9 isocyanate derivatives. Calibration curves were established with a range of 0.05 to 1.4 µg ml^{-1} and dilutions were performed in accordance with the ASSET™ protocol. However, the dilution protocol relies on a separately prepared and extracted sample containing only the internal standard. Recoveries of the internal standard were found to be highly variable [(Range 10,188-50,213 area counts), (Median: 21,117 area counts), (RSD: 51)]. The high variability in the internal standard extraction introduces bias into diluted sample results. For this study, 19 of 32 ASSET™ samples were diluted. It is important to note that as of January 2014, Sigma-Aldrich Co. LLC has made available HDI oligomer and monomer standards with higher concentrations (~200-300 µg ml^{-1}) that would address this limitation.

3.3.6 *Flow Rate Differences*

An additional aim of this research was to compare a full shift ASSET™ sampler with the partial shift ASSET™ sample and partial shift ISO-CHEK®. To accomplish this, two ASSET™ samplers were connected to a single SKC AirChek 2000 air sampling pump using a wye-connection during 4 of the 6 shifts sampled. The air sampling pump was pre-calibrated to a flow rate of 0.2 l min^{-1} through each of the two ASSET™ samplers using low-flow adapters connected in series to two Bios DryCal Defender 510 Primary Flow calibrators. Post-calibration of the sampling pumps reported flow rate percent differences of 5.3 to 10.6 percent, significantly greater than the recommended 5 percent for acceptability. The wye-connector was relocated after the first shift in an attempt to correct the flow rate differences; however, pre- and post-calibration values remained high after the second shift. For the third shift, the wye-connector was removed and a single ASSET™ sample was connected to the SKC AirChek 2000 pump. Flow rate differences (3.5 and 1.4 percent) were below 5 percent and the issue was resolved. Refer to Table 11 for a comparison of per- and post-sampling flow rates. It appears the ASSET™ sampler struggled to maintain a balanced flow in the two branches following the wye-connection. The percent difference in each individual branch varied significantly pre- and post-sampling; however, the combined flow in both branches appeared more stable and closer to the 5 percent criterion. Twenty-one of the 32 samples used in the paired *t*-test were collected using the wye-connection and had pre- and post sampling flow rate differences greater than 5 percent.

Table 11. ASSET™ Sampler Pre- and Post-Sampling Flow Rates

Pump	**Pump S/N**	**Sample**	**Pre-Calibration (l min^{-1})**	**Post-Sampling (l min^{-1})**	**Percent Difference**
Day 1, Worker 1	08575	Full Shift Sampler	0.20019	0.22464	11.5
		Partial Shift Sampler	0.20222	0..18264	-10.2
		Combined Flow	*0.4024*	*0.4073*	*1.2*
Day 1, Worker 2	08584	Full Shift Sampler	0.20058	0.18934	-5.8
		Partial Shift Sampler	0.20122	0.19086	-5.3
		Combined Flow	*0.4018*	*0.3802*	*-5.5*
Day 2, Worker 1	08584	Full Shift Sampler	0.20707	0.23783	13.8
		Partial Shift Sampler	0.19577	0.18317	-6.7
		Combined Flow	*0.4028*	*0.4210*	*4.4*
Day 2, Worker 2	08575	Full Shift Sampler	0.20383	0.20148	-1.2
		Partial Shift Sampler	0.20936	0.18834	-10.6
		Combined Flow	*0.4132*	*0.3898*	*-5.8*

3.4 SIGNIFICANCE OF FINDINGS

Research findings indicate ASSET™ samplers have the potential to collect a statistically significant higher level of HDI monomer and oligomers. Additional research is required to fully test the adequacy of the sampling apparatus and analytical method to determine if it is a suitable substitute for the ISO-CHEK® method when determining employee breathing zone concentrations during US Air Force industrial operations. This research also indicates isocyanate exposures may be underestimated using the ISO-CHEK® protocol. The ASSET™ sampler, if adopted by the USAF following additional research, may provide a better field solution for industrial hygiene personnel to help ensure compliance and protection of worker health while using isocyanate-based corrosion control materials.

3.5 FUTURE RESEARCH

Robust testing of the ASSET™ sampler specifically for collection and analysis of HDI oligomers is required. Future research should address the limitations identified in this study as well as the testing requirements recommended in the NIOSH Technical Report, *Guidelines for Air Sampling and Analytical Method Development and Evaluation* to include:

- Air sampler capacity
- Air sampler performance under varying environmental parameters
- Sample stability (currently underway as an extension of this research)
- Precision, bias, and accuracy (NIOSH, 1995)

Future research efforts may also expand ASSET^{TM} evaluation to include the second most common isocyanate used in the US Air Force, methylene bisphenyl diisocyanate (MDI). MDI accounts for nearly 10 percent of the remaining isocyanate usage after HDI (85%) in the US Air Force. Additional research may be expanded to include the use of an HPLC/MS-MS using multiple reaction monitoring (MRM) detection. Lastly, if the limitations previously identified are addressed, repetition of this research would be beneficial and may increase confidence in study findings.

APPENDIX A. EXPANDED LITERATURE REVIEW

This expanded literature review provides additional background information illustrating the significance of the problem statement and objectives of this thesis. A summary of the toxicology studies constituting the current body of knowledge of exposures to isocyanates is included. Additionally, current occupational exposure limits and their basis are discussed.

A.1 TOXICOLOGY

Monomeric HDI has a high vapor pressure causing it to vaporize quickly at room temperature leading to inhalation and dermal risks to industrial workers. Monomeric HDI, like oligomeric HDI, can cause local irritation to the nasal and respiratory tract. Asthma-like conditions can be induced in sensitized people at extremely low concentrations, as low as 0.2 ppb. Monomeric HDI also produces clinical signs of respiratory toxicity that are similar to other diisocyanates (e.g. toluene diisocyanate, TDI). At concentrations greater than 0.6 ppb, exposure effects can include irritation of the nose, throat, and mucous membranes of the lungs as well as cough, laryngitis, bronchitis, tightness of the chest, hoarseness, pulmonary edema, and emphysema. Other clinical signs may include more vague symptoms, such as headache and fatigue (Abadin and Spoo, 1998).

HDI oligomers, specifically HDI biuret and trimer, can induce respiratory and immunological reactions similar to HDI monomer in both humans and animals. Unlike monomeric HDI, polymeric forms typically have a very low vapor pressure, making vaporization at room temperature unlikely. Polymeric HDI exposures occur when the paint/hardener combination is ejected from the spray nozzle onto the painted surface. Current HVLP technology has transfer efficiency between 60 to 85 percent, leaving the remaining droplets to be captured by the airflow around the surface. During the spraying process, aerosol droplets of polymeric HDI suspended in the surrounding air are breathed in by or lands on the skin of the exposed worker (NIOSH, 1996).

A.1.2 Health Effects by System

The actual data on specific organ and system effects of HDI are limited. HDI is toxic by all routes of exposure, although inhalation is the most common form of exposure in the aerospace and defense industry. Most diisocyanates have not been extensively tested for carcinogenic potential, including HDI. One report found HDI was not carcinogenic by inhalation after a two year repeated dose study in rats (Abadin and Spoo, 1998). HDI is not a known mutagen or teratogen (EPA, 2012). Several studies have reported respiratory irritation, including burning and irritation to the nasal tract, throat, and chest after inhalation exposure. The exact mechanism of action for producing irritation is unknown, but is likely related to their high reactivity with biological macro-molecules and various body proteins. Most isocyanates are also considered to be potential respiratory tract sensitizers. The mechanisms involving sensitization are also unknown (Abadin and Spoo, 1998).

The main organ system affected by HDI is the respiratory system. Exposure may lead to hypersensitivity reactions and irritations. Four specific effects to respiratory health have been identified: occupational asthma with a latency period, occupational asthma without a latency period (irritant-induced asthma and reactive airway dysfunction syndrome (RADS)), hypersensitivity pneumonitis or extrinsic allergic alveolitis, and chronic obstructive pulmonary disease (COPD). Most literature focuses on the first two diseases related to occupational asthma as the main health effect related to HDI exposure; isocyanates as a group are reported as the number one cause of occupational asthma (Nordic Council of Ministers, 2001). Concentration dependent effects occur, often after a delay of 4 to 8 hours and may persist for 3 to 7 days. High-concentration inhalation can lead to chest tightness, cough, breathlessness, wheezing, and inflammation of the bronchi and sputum production. Accumulation of fluid in the lungs can also occur. Previously exposed personnel may develop inflammation of the lungs when re-exposed to extremely low levels of HDI. Flu-like symptoms such as fever, malaise, shortness of breath, and cough can develop 4 to 6 hours after exposure and persist for 12 hours or longer. In sensitized individuals, asthmatic attacks can occur after exposure to extremely low HDI concentrations. Asthmatic reactions can be immediate, delayed, or both. Exposure to HDI can lead to Reactive Airway Dysfunction Syndrome (RADS), a chemically, or irritant-induced type of asthma.

While isocyanates mainly impact respiratory system function, additional effects have been documented in other organ systems. Acute exposure to high levels of HDI vapor has been linked to central nervous system effects including lightheadedness, headache, insomnia, mental aberrations, impaired gait, loss of consciousness, and coma. As mentioned previously, HDI is a dermal hazard causing severe skin irritation. Skin contact may also result in respiratory sensitization. HDI is an ocular hazard; exposure can cause eye irritation, inflammation of the eye membrane, inflammation of the cornea, clouding of the eye surface, and secondary glaucoma. HDI exposure can affect the blood, leading to mild leucocytosis without eosinophilia. The bone marrow does not appear to be affected. Animal studies indicate the gastrointestinal tract is not a target organ system for HDI toxicity. No effects have been reported for the liver, kidney, or the reproductive systems (Abadin and Spoo, 1998).

A.1.3 Health Effects by Route of Exposure - Inhalation

When inhaled, HDI binds to human tissues, proteins, and DNA forming toxic adducts and metabolites. The inhalation reference concentration (RfC) for HDI is 0.01 $\mu g\ m^{-3}$ based on the degeneration of olfactory epithelium in rats. The RfC is an estimate of a continuous inhalation exposure to the human population that is likely to be without appreciable risk of deleterious noncancer effects during a lifetime (EPA, 2007). Acute animal tests in rats have shown HDI to have extreme acute toxicity from inhalation exposure. No studies were located regarding death in humans after acute inhalation exposure to HDI. Several reports of death after inhalation exposures of acute-duration in laboratory animals have been recorded by the Agency for Toxic Substance and Disease Registry (Abadin and Spoo, 1998). In addition to acute toxicity, epidemiological studies have suggested that chronic exposure to HDI may cause chronic lung problems. Animal studies have reported effects on nasal tissue, reparatory tract, and lungs from chronic inhalation of HDI (EPA, 2007). A brief summary of the lethal doses (LD_{50}), No-Observed-Adverse-Reaction Level (NOAEL), and the Lowest-Observed-Adverse-

Reaction Level (LOAEL) for both acute and chronic inhalation studies are listed in Table 12 for various animals and exposure durations.

Table 12. Levels of Significant Exposure to HDI – Inhalation

(Abadin and Spoo, 1998)

Species	**Exposure Duration**	**NOAEL**	**LOAEL**	**LD$_{50}$**
Acute Exposures				
Rats	6 hr 4-8 hr	- 5 ppm	3 ppm 11 ppm	44 ppm -
Guinea Pig	2-6 hr	0.5 ppm	1.8 ppm	4 ppm
Human	5 min	-	0.02 ppm	-
Chronic Exposures				
Human	7 yrs	-	0.0001 ppm	-
Rat	1 and 2 yrs 5 d/wk, 6 hr/d	0.175 ppm	0.175 ppm	-

A.1.4 Health Effects by Route of Exposure - Dermal

Dermal exposure due to HDI may occur by immersion, surface contact, deposition of aerosol, or by the uptake of vapor through the skin and may constitute an important route of exposure (Abadin and Spoo, 1998). Acute dermal exposure to isocyanates has been linked to allergic contact dermatitis in humans and respiratory sensitization in animals. Chronic dermal exposure has resulted in skin irritation and sensitization in guinea pigs, rabbits, and mice. Although dermal absorption is thought to be slow, HDI reacts with the skin proteins to produce a tanning effect (EPA, 2007). Levels of significant dermal exposure as recorded by the ATSDR are summarized in Table 13.

Table 13. Levels of Significant Exposure to HDI - Dermal

(Abadin and Spoo, 1998)

Species	Exposure Duration	NOAEL	LOAEL	LD_{50}
Acute Exposures				
Mouse	Once	-	0.2 mg/kg	2800 mg/kg
Guinea Pig	Once	0.01%	0.1%	-
Intermediate Exposures				
Guinea Pig	3 wk, 9 x	0.05%	0.5%	-

A.2 TOXICOKINETICS

The mechanisms for the development of HDI induced asthma have not yet been elucidated, but it seems that different immunological, irritative and toxic mechanisms are involved (Raulf-Heimsoth and Baur 1998). Since the toxicokinetics of HDI are unknown, some researchers have turned to similar studies for Toluene Diisocyanate (TDI) as a surrogate model for HDI (von Burg, 1993). Controversy remains regarding the toxicokinetic similarity of the two isocyanates; however, in the absence of HDI literature some of the following toxicokinetic discussion has been extrapolated from exposures to TDI.

A.2.1 Absorption

Little information is available in the literature on the absorption of HDI after inhalation, oral, or dermal exposure. Referencing TDI, animal inhalation studies demonstrated TDI is mainly absorbed in the central respiratory passages and far out in the bronchioles. It is found in the epithelium and at the sub epithelial level from the nose down to the terminal bronchioles. It generally binds to proteins quite rapidly.

Isocyanates react quickly in the body forming adducts. Studies suggest the toxicity of isocyanates is due to the distribution of isocyanate-glutathione conjugates to various organs via blood and the release of free isocyanate in peripheral tissues. The mechanism of distribution of isocyanates in the human body is largely unknown, no information was found in the literature (Nakashima, 2002; Nordic Council of Ministers, 2001).

A.2.2 Metabolism

Information on the metabolism of isocyanates is limited. The major metabolite of HDI in humans is 1,6-hexamethylene diamine (HAD). No information was located in the available literature specifically addressing HAD after inhalation, oral, or dermal exposures (Abadin and Spoo, 1998).

A.2.3 Elimination and Excretion

Multiple studies have demonstrated HDI metabolites, HAD, are excreted through the urine. In a 7.5-hour inhalation study of humans, HAD was excreted almost immediately through the urine with levels undetectable 15 hours post exposure (Abadin and Spoo, 1998).

A.3 OCCUPATIONAL EXPOSURE LIMITS

Two approaches are currently used to express OELs for isocyanates. The most common approach is to describe the OEL for individual isocyanates as either parts per million (ppm) or micrograms per cubic meter of air ($\mu g\ m^{-3}$). The OEL for the monomeric form of HDI is expressed in this manner by OSHA, NIOSH, and American Conference of Governmental Industrial Hygienist (ACGIH). With the exception of Oregon OSHA (OR-OSHA), no US exposure setting agency has established an OEL for individual oligomers. This is of particular concern since coatings used in aerospace are primarily composed of the oligomer form of HDI. The OR-OSHA HDI oligomer short-term exposure level ($STEL_{15min}$) is 1,000 μg m^{-3} and the 8-hour time-weighted average (TWA) permissible exposure limit is 500 μg m^{-3}. The OR-OSHA OELs were promulgated in 1986 and are derived from animal toxicity studies with exposure to HDI isocyanurate and HDI biuret.

The second approach expresses the OEL in terms of the total number of NCO groups within an isocyanate mixture, rather than quantifying each individual species. This OEL is expressed as the mass of total NCO groups or as "μg NCO m^{-3}" and may be referred to as the Total Reactive Isocyanate Group (TRIG). United Kingdom Health and Safety Executives (UK-HSE) $STEL_{15min}$ standard for total NCO is 70 μg NCO m^{-3} for all isocyanates. The UK-HSE STEL was established in 1983 and includes monomers and oligomers of all isocyanates, regardless of their individual identities or toxicities. The UK-HSE is derived from the ACGIH's TLV for monomeric TDI, which is 0.02 ppm (equivalent to 142 μg m^{-3} with 48% of molecular weight as NCO). Because the UK-HSE STEL is based on the toxicological characteristics of TDI monomer, it may not be directly applicable to exposures during spray applications, where the predominant isocyanate species in the paint is HDI (Reeb-Whitaker and others, 2012). Refer to Table 14 for a summary of the varying OELs established by national and international standard setting agencies, of particular interest is the order of magnitude difference in the TRIG standard compared to the OR-OSHA standard.

During its health hazard evaluations NIOSH has utilized, and the US Air Force School of Aerospace Medicine supports, the use of the OR-OSHA permissible exposure limit of 500 µg m^{-3} for an 8-hour TWA and 1,000 µg m^{-3} as a STEL for comparison of HDI polyisocyanate results. The ACGIH TLV 8-hour TWA of 34 µg m^{-3} is recommended for monomers (Batten, 2012).

Table 14: Current US, UK, and Swedish OELs for HDI

(Adapted from Bello and others, 2004)

		HDI Monomer	**HDI Polyisocyanate**	**TRIG**[a]
OSHA PEL	*TWA 8-hr*	-	-	-
	Ceiling	-	-	-
NIOSH REL	*TWA 10-hr*	35	-	-
	Ceiling 10 min	140	-	-
ACGIH TLV	*TWA 8-hr*	34	-	-
	STEL 15 min	-	-	-
Oregon OSHA	*TWA 8-hr*	-	500	-
	STEL 15 min	-	1,000	-
UK-HSE OEL	*TWA 8-hr*	-	-	(20)
	Ceiling 10 min	-	-	(70)
Swedish OEL	*TWA 8-hr*	-	-	(20)[b]
	STEL 5 min	-	-	(44)[b]

Bracketed values represent the equivalent standard in µg NCO/m^3

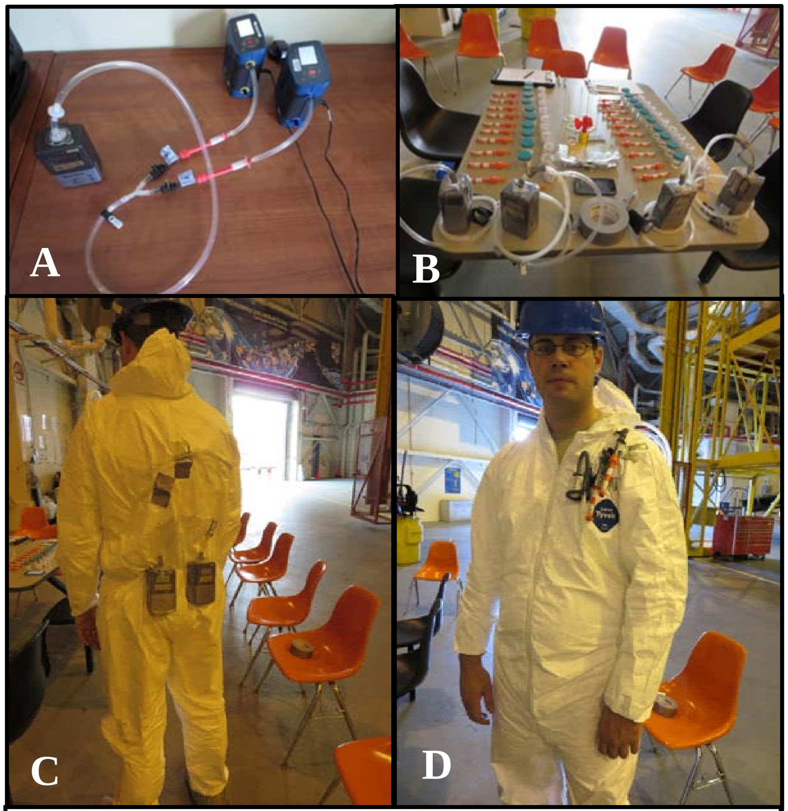
[a] Total reactive isocyanate group (TRIG) in µg/m^3. The standard applies to all isocyanate species (monomers, polyisocyanates, and their mixtures) regardless of their origin.

[b] The Swedish OEL is based on 5 ppb (TWA), which equals 90 µg HDI-biuret/m^3 (20 µg NCO/m^3), and a 5-min STEL of ~ 13 ppb, which equals 200 µg HDI-biuret/m^3 (44 µg NCO/m^3)

APPENDIX B. EXPANDED RESULTS AND DISCUSSIONS

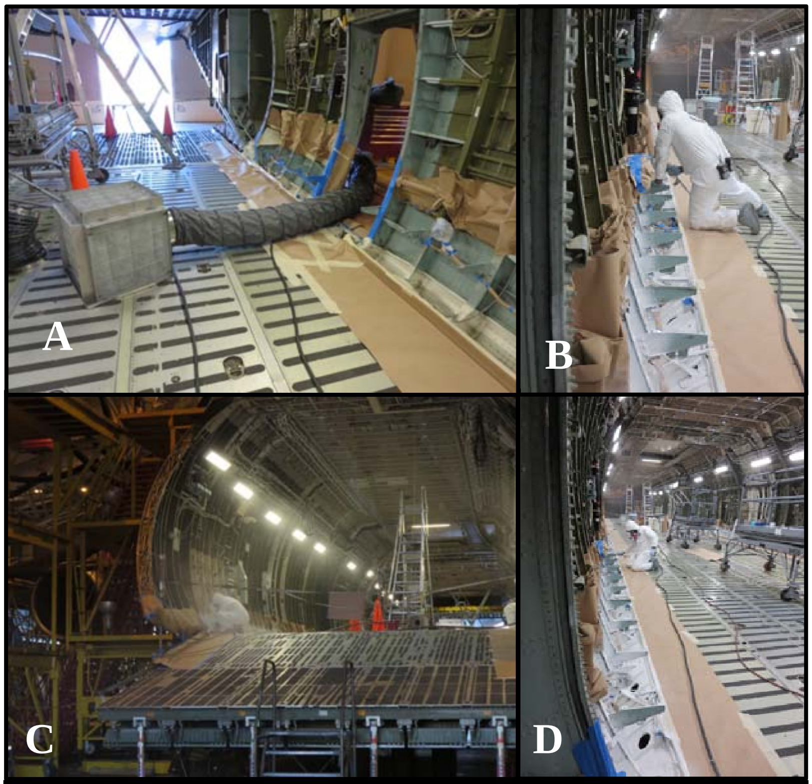
This appendix supplements the Results and Discussion sections in Chapter II. The material presented in this appendix was deemed excessive for a prospective article for publication. It includes pictures from the painting process, detailed analytical results, and additional laboratory quality control documentation.

B.1 SAMPLE COLLECTION – PAINTING PROCESS PICTURES



Sample Collection. A) Calibration of partial shift and full shift ASSET samplers using low flow adapters and Bios DryCal calibrator; B) Sample staging area; C) Rear sampling pump configuration; D) Front sampling media configuration including 2 ASSET samplers and 1 Iso-Chek cassette.

Figure 9. Sample Collection



Painting Process. A) Portable air handler with filters; B-D) Chine cove painting with HVLP spray gun

Figure 10. Painting Process

Finished Product. A) Painted troop galley; B) Painted chine coves

Figure 11. Painted Troop Galley and Chine Coves

B.2 QUANTIFICATION OF ISOCYANATES BY HPLC-MS

B.2.1 HPLC-MS Calibration Curves

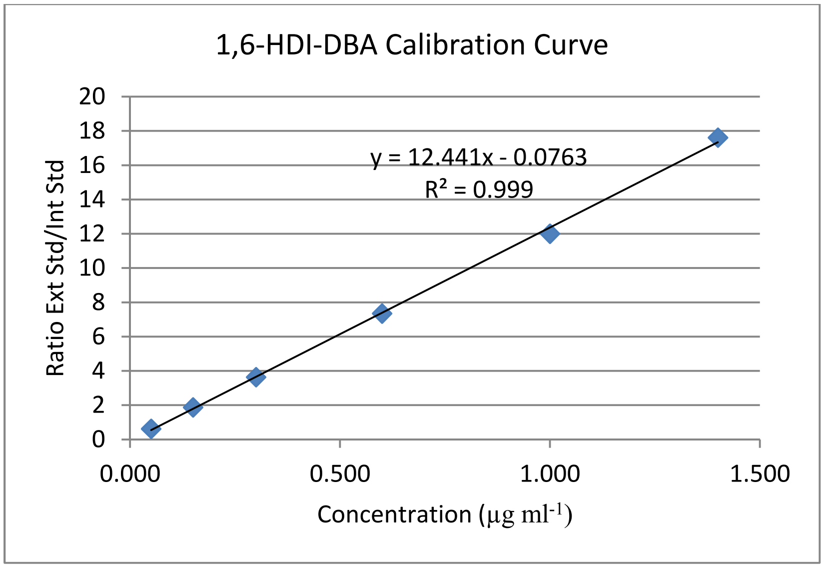


Figure 12. 1,6-HDI-DBA Calibration Curve, $R^2 = 0.999$

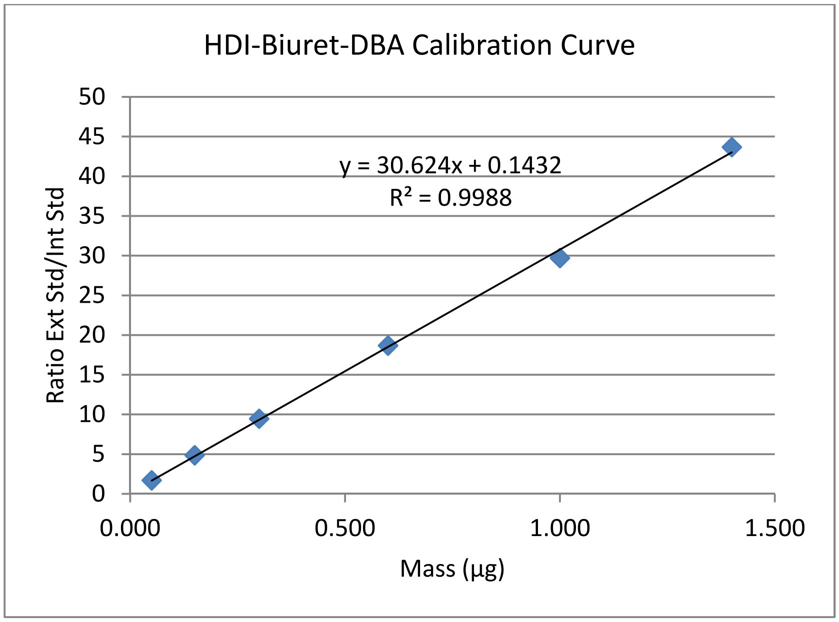


Figure 13. HDI-Biuret-DBA Calibration Curve, $R^2 = 0.9988$

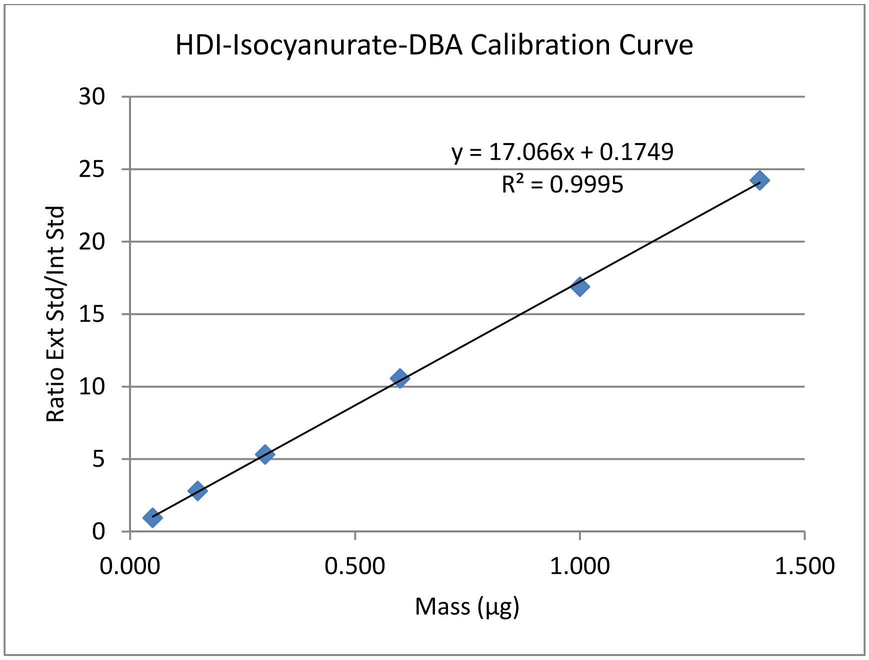


Figure 14. HDI-Isocyanurate-DBA Calibration Curve, $R^2 = 0.9995$

B.2.2 Media Spike Recovery Study

Table 15. HDI-DBA Media Spike Recoveries

HDI-DBA					
Spike ID	Replicate	Target Concentration µg	Analyzed Concentration µg	Recovery %	Statistics
Media Spike	1	0.10	0.1044	104.4%	**Mean**
Media Spike	2	0.15	0.1568	104.5%	**99.4%**
Media Spike	3	0.30	0.3000	100.0%	
Media Spike	4	0.50	0.4914	98.3%	**STD Dev**
Media Spike	5	0.60	0.5884	98.1%	**3.41%**
Media Spike	6	0.80	0.7782	97.3%	
Media Spike	7	1.00	0.9608	96.1%	**%RSD**
Media Spike	8	1.20	1.1539	96.2%	**3.43**

Table 16. HDI-Biuret-DBA Media Spike Recoveries

HDI-Biuret-DBA

Spike ID	Replicate	Target Concentration µg	Analyzed Concentration µg	Recovery %	Statistics
Media Spike	1	0.10	0.1047	104.7%	**Mean**
Media Spike	2	0.15	0.1462	97.5%	**100.6%**
Media Spike	3	0.30	0.2919	97.3%	
Media Spike	4	0.50	0.5071	101.4%	**STD Dev**
Media Spike	5	0.60	0.5778	96.3%	**5.18%**
Media Spike	6	0.80	0.8087	101.1%	
Media Spike	7	1.00	0.9554	95.5%	**%RSD**
Media Spike	8	1.20	1.3304	110.9%	**5.15**

Table 17. HDI-Isocyanurate-DBA Media Spike Recoveries

HDI-Isocyanurate-DBA

Spike ID	Replicate	Target Concentration µg	Analyzed Concentration µg	Recovery %	Statistics
Media Spike	1	0.10	0.0867	86.7%	**Mean**
Media Spike	2	0.15	0.1148	76.5%	**83.1%**
Media Spike	3	0.30	0.2199	73.3%	
Media Spike	4	0.50	0.4320	86.4%	**STD Dev**
Media Spike	5	0.60	0.5034	83.9%	**6.83%**
Media Spike	6	0.80	0.6917	86.5%	
Media Spike	7	1.00	0.7720	77.2%	**%RSD**
Media Spike	8	1.20	1.1269	93.9%	**8.22**

B.2.3 ASSET^{TM} Sampler Results

Table 18. ISO-CHEK$^{®}$ and ASSET^{TM} HDI Monomer Concentrations

IsoChek Sample ID	ISO-CHEK Monomer Concentration (mg m-3)	ASSET Sample ID	ASSET Monomer Concentration (mg m^{-3})	Sample used in paired *t*-test?	Comments
1C01	<0.0187	D1B01	Lab Error	N	ASSET Sampler Lab Error
1C02	<0.0187	D1B02	Lab Error	N	ASSET Sampler Lab Error
1C03	<0.0187	D1B03	Lab Error	N	ASSET Sampler Lab Error
1C04	<0.0187	D1B04	Lab Error	N	ASSET Sampler Lab Error
1C05	<0.0187	D1B05	Lab Error	N	ASSET Sampler Lab Error
1C06	<0.0187	D1B06	Lab Error	N	ASSET Sampler Lab Error
1C07	<0.0187	D1B07	Lab Error	N	ASSET Sampler Lab Error
1C08	<0.0187	D1B08	Lab Error	N	ASSET Sampler Lab Error
D2C01	0.0191	2B01	0.0870	Y	
D2C02	0.0522	2B02	0.1050	Y	
D2C03	0.0267	2B03	0.0480	Y	
D2C04	0.0843	2B04	Lab Error	N	ASSET Sampler Lab Error
D2C05	<0.0092	2B05	<0.0088	Y	
D2C06	<0.0185	2B06	<0.0177	Y	
D2C07	<0.0185	2B07	<0.0177	Y	
D2C08	<0.0185	2B08	<0.0177	Y	
10C01	<0.0189	10B01	<0.0159	Y	
10C02	<0.0189	10B02	0.0350	Y	
10C03	0.0591	10B03	Lab Error	N	ASSET Sampler Lab Error
10C04	0.0223	10B04	0.0710	Y	
10C05	<0.0189	10B05	<0.0159	Y	
10C06	<0.0189	10B06	<0.0159	Y	
20C01	<0.0189	20B01	<0.0166	Y	
20C02	0.0409	20B02	0.2670	Y	
20C03	0.0417	20B03	0.2010	Y	
20C04	<0.0189	20B04	<0.0166	Y	
20C05	<0.0189	20B05	0.0360	Y	
20C06	<0.0189	20B06	<0.0166	Y	
2C01	<0.0185	1B01	<0.0183	Y	
2C02	<0.0185	1B02	0.0250	Y	
2C03	<0.0185	1B03	0.0480	Y	
2C04	<0.0185	1B04	Lab Error	N	ASSET Sampler Lab Error
2C05	<0.0185	1B05	0.0630	N	Hose disconnected from IsoChek
2C06	<0.0185	1B06	0.0500	Y	
2C07	0.0190	1B07	0.0980	Y	
2C08	0.0275	1B08	0.0890	Y	
2C09	<0.0278	1B09		N	ASSET Sampler lost during collection
2C10	0.0286	1B10	<0.2738	N	ASSET Pump failed at 1 minute
2C11	<0.0185	1B11	0.0830	N	ASSET Pump failed at 2 minutes
2C12	0.0295			N	No corresponding ASSET sample
4C01	<0.0182	3B01	<0.0175	Y	
4C02	<0.0182	3B02	<0.0175	N	Pump malfunctioned
4C03	<0.0182	3B03	0.0250	Y	
4C04	<0.0182	3B04	<0.0175	Y	
4C05	0.0225	3B05	0.0570	Y	
4C06	<0.0273	3B06	0.0420	Y	
4C07	<0.0182	3B07	0.0210	N	ISO-CHEK pump disconnected sampling
4C08	0.0204	3B08	0.0330	Y	
4C09	<0.0182	3B09	0.0320	Y	
4C10	<0.0182	3B10	0.0240	Y	
		2A01	0.0560	N	
		3A01	Lab Error	N	ASSET Sampler Lab Error

Table 19. ISO-CHEK and ASSET HDI Oligomer Concentrations

IsoChek Sample ID	ISO-CHEK Oligomer Concentration (mg m^{-3})	ASSET Sample ID	Dilution Factor	ASSET Oligomer Concentration (mg m^{-3})	Sample used in paired *t*-test?	Comments
1C01	0.1230	D1B01		Lab Error	N	ASSET Sampler Lab Error
1C02	0.8070	D1B02		Lab Error	N	ASSET Sampler Lab Error
1C03	0.7470	D1B03		Lab Error	N	ASSET Sampler Lab Error
1C04	0.2050	D1B04		Lab Error	N	ASSET Sampler Lab Error
1C05	0.2240	D1B05		Lab Error	N	ASSET Sampler Lab Error
1C06	0.0541	D1B06		Lab Error	N	ASSET Sampler Lab Error
1C07	<0.0334	D1B07		Lab Error	N	ASSET Sampler Lab Error
1C08	<0.0334	D1B08		Lab Error	N	ASSET Sampler Lab Error
D2C01	4.5900	2B01	100	7.4070	Y	
D2C02	1.7000	2B02	100	18.8020	Y	
D2C03	3.0900	2B03	10	5.4650	Y	
D2C04	0.8730	2B04		Lab Error	N	ASSET Sampler Lab Error
D2C05	0.3470	2B05		0.0190	Y	
D2C06	<0.0330	2B06		0.0210	Y	
D2C07	<0.0330	2B07		<0.0177	Y	
D2C08	<0.0330	2B08		<0.0177	Y	
10C01	<0.0337	10B01		<0.0159	Y	
10C02	2.7200	10B02	100	9.3060	Y	
10C03	1.1300	10B03		Lab Error	N	ASSET Sampler Lab Error
10C04	3.7238	10B04		3.5150	Y	
10C05	0.0342	10B05		0.0280	Y	
10C06	<0.0337	10B06		<0.0159	Y	
20C01	<0.0337	20B01		<0.0166	Y	
20C02	1.7600	20B02	1000	76.5400	Y	
20C03	1.8300	20B03	1000	44.3090	Y	
20C04	0.2610	20B04		0.0830	Y	
20C05	2.7200	20B05	100	6.9740	Y	
20C06	0.1100	20B06		0.0390	Y	
2C01	<0.0330	1B01		<0.0183	Y	
2C02	3.0400	1B02	10	3.0540	Y	
2C03	3.8300	1B03	100	7.5090	Y	
2C04	1.8500	1B04		Lab Error	N	ASSET Sampler Lab Error
2C05	5.6200	1B05	100	19.8100	N	IsoChek hose disconnected
2C06	4.3200	1B06	100	9.6390	Y	
2C07	4.8800	1B07	100	24.5980	Y	
2C08	5.7900	1B08	100	20.9760	Y	
2C09	<0.0496	1B09			N	ASSET lost during collection
2C10	3.1400	1B10	10	10.9820	N	ASSET Pump failed at 1 min
2C11	<0.0330	1B11	10	4.5800	N	ASSET Pump failed at 2 min
2C12	4.1500				N	No correspond ASSET sample
4C01	<0.0326	3B01		0.0190	Y	
4C02	2.1000	3B02	10	0.7690	N	Pump malfunctioned
4C03	3.4800	3B03	10	1.4680	Y	
4C04	<0.0326	3B04		<0.0175	Y	
4C05	3.2900	3B05	10	4.3460	Y	
4C06	5.5100	3B06	10	3.1030	Y	
4C07	<0.0326	3B07	10	2.0100	N	ISO-CHEK hose disconnected
4C08	2.4400	3B08	10	3.2370	Y	
4C09	3.9500	3B09	10	2.6120	Y	
4C10	2.8600	3B10	10	3.8860	Y	
		2A01	1000	16.3960	N	
		3A01		Lab Error	N	ASSET Sampler Lab Error

B.3 QUANTIFICATION OF ISOCYANATES BY HPLC-UV

The following pages contain the results for the ISO-CHEK® samples analyzed by the US Air Force School of Aerospace Medicine Occupational and Environmental Health Industrial Hygiene laboratory.

MEMORANDUM FOR: Capt Tiffany Heline 14 January 2014
88 AMDS/SGPB
2325 5th Street, Bldg 675
WRIGHT-PATTERSON AFB, OH 454337

FROM: USAFSAM OE Industrial Hygiene
2510 Fifth Street, Bldg 20840, Room W327
Wright Patterson Air Force Base, OH 45433-7913

REF: Order No.: S1310016

Dear Capt Tiffany Heline:

Enclosed are the sample reports from 30 samples received on 10/2/2013.

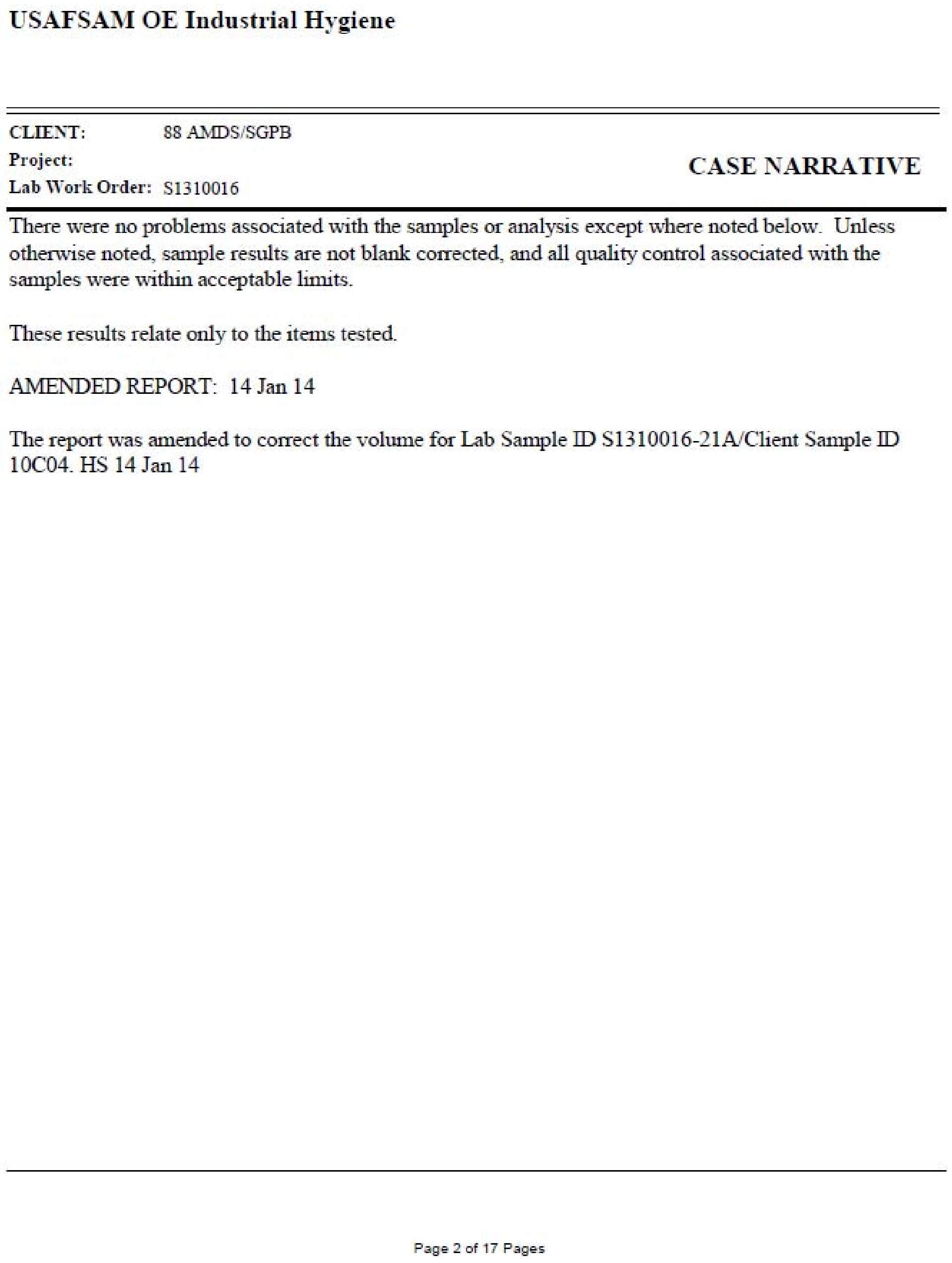
Samples, not consumed in analysis, will be held according to the appropriate regulatory authority unless you specifically request otherwise. Should you choose to reproduce this report, we recommend you do so in its entirety so that the integrity of the data package is kept intact.

If you have questions, or if we may be of further assistance to you, please do not hesitate to contact us.

Sincerely,

ERIC L WEATHERHOLT, Capt, USAF
Analytical Services Program Manager
Tel: (937) 938-2523 (DSN Prefix: 798)
https://kx.afms.mil/chemlab

Note: Sample analysis performed by: USAFSAM/OE Chemistry Division



USAFSAM OE Industrial Hygiene

CLIENT:	88 AMDS/SGPB
Project:	
Lab Work Order:	S1310016

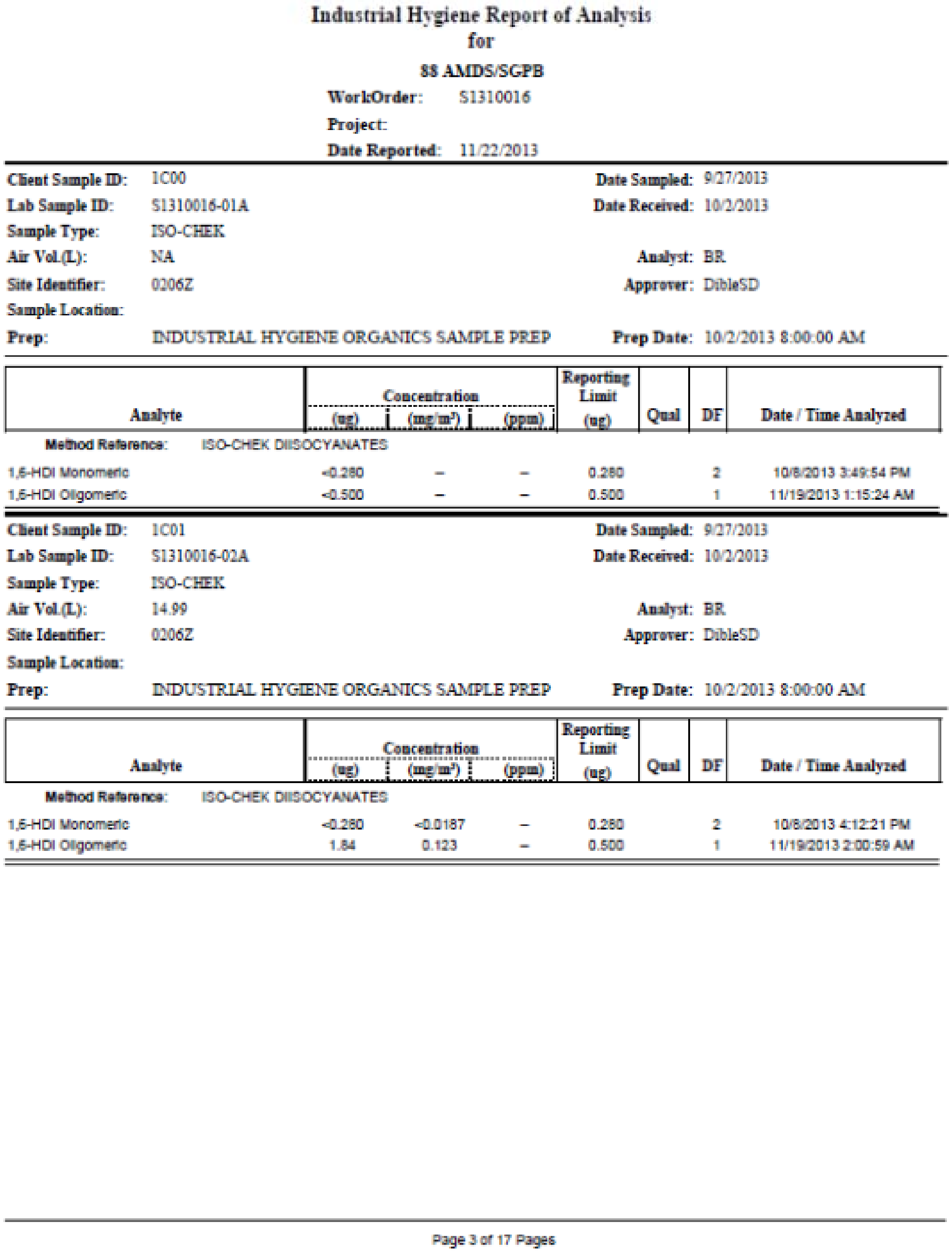
CASE NARRATIVE

There were no problems associated with the samples or analysis except where noted below. Unless otherwise noted, sample results are not blank corrected, and all quality control associated with the samples were within acceptable limits.

These results relate only to the items tested.

AMENDED REPORT: 14 Jan 14

The report was amended to correct the volume for Lab Sample ID S1310016-21A/Client Sample ID 10C04. HS 14 Jan 14



Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310016
Project:
Date Reported: 11/22/2013

Client Sample ID: 1C00 **Date Sampled:** 9/27/2013
Lab Sample ID: S1310016-01A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): NA **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location:
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	Concentration (mg/m³)	Concentration (ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	–	–	0.280		2	10/8/2013 3:49:54 PM
1,6-HDI Oligomeric	<0.500	–	–	0.500		1	11/19/2013 1:15:24 AM

Client Sample ID: 1C01 **Date Sampled:** 9/27/2013
Lab Sample ID: S1310016-02A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 14.99 **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location:
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	Concentration (mg/m³)	Concentration (ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0187	–	0.280		2	10/8/2013 4:12:21 PM
1,6-HDI Oligomeric	1.84	0.123	–	0.500		1	11/19/2013 2:00:59 AM

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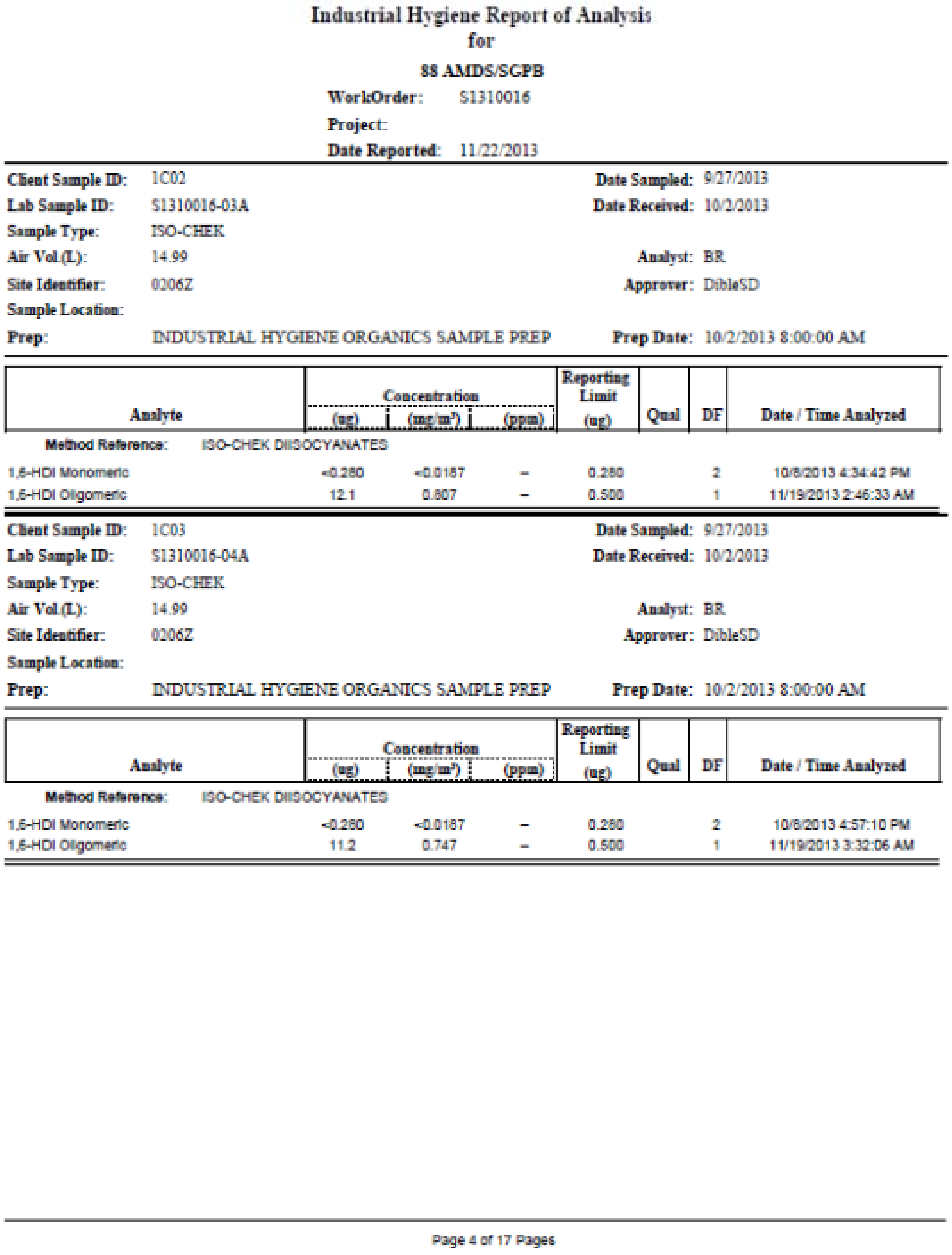

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310016
Project:
Date Reported: 11/22/2013

Client Sample ID:	1C02	**Date Sampled:**	9/27/2013
Lab Sample ID:	S1310016-03A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	14.99	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:			
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	(mg/m³)	(ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0187	--	0.280		2	10/8/2013 4:34:42 PM
1,6-HDI Oligomeric	12.1	0.807	--	0.500		1	11/19/2013 2:46:33 AM

Client Sample ID:	1C03	**Date Sampled:**	9/27/2013
Lab Sample ID:	S1310016-04A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	14.99	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:			
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	(mg/m³)	(ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0187	--	0.280		2	10/8/2013 4:57:10 PM
1,6-HDI Oligomeric	11.2	0.747	--	0.500		1	11/19/2013 3:32:06 AM

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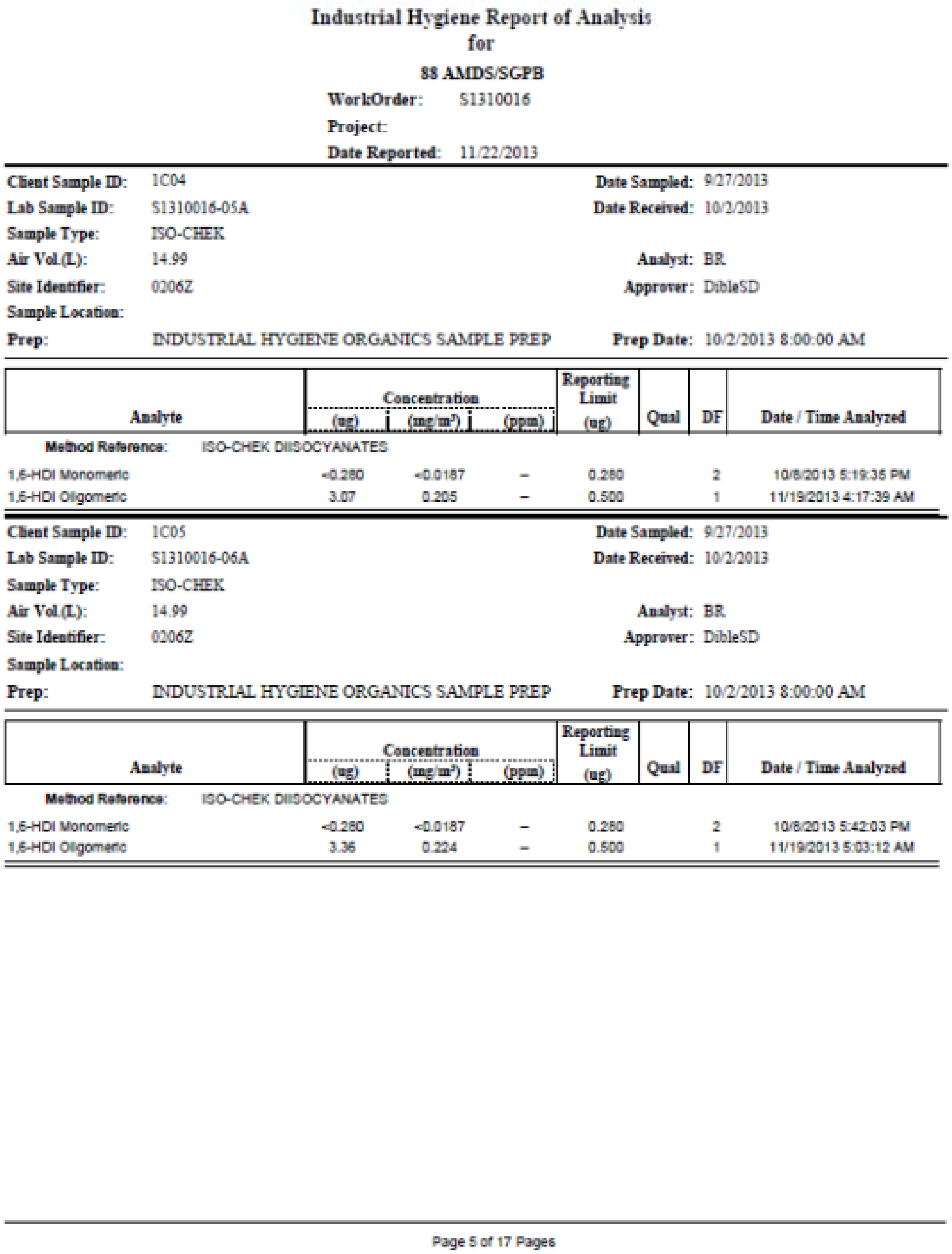

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310016
Project:
Date Reported: 11/22/2013

Client Sample ID:	1C04	**Date Sampled:**	9/27/2013
Lab Sample ID:	S1310016-05A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	14.99	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:			
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	Concentration (mg/m³)	Concentration (ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0187	--	0.280		2	10/8/2013 5:19:35 PM
1,6-HDI Oligomeric	3.07	0.205	--	0.500		1	11/19/2013 4:17:39 AM

Client Sample ID:	1C05	**Date Sampled:**	9/27/2013
Lab Sample ID:	S1310016-06A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	14.99	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:			
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	Concentration (mg/m³)	Concentration (ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0187	--	0.280		2	10/8/2013 5:42:03 PM
1,6-HDI Oligomeric	3.36	0.224	--	0.500		1	11/19/2013 5:03:12 AM

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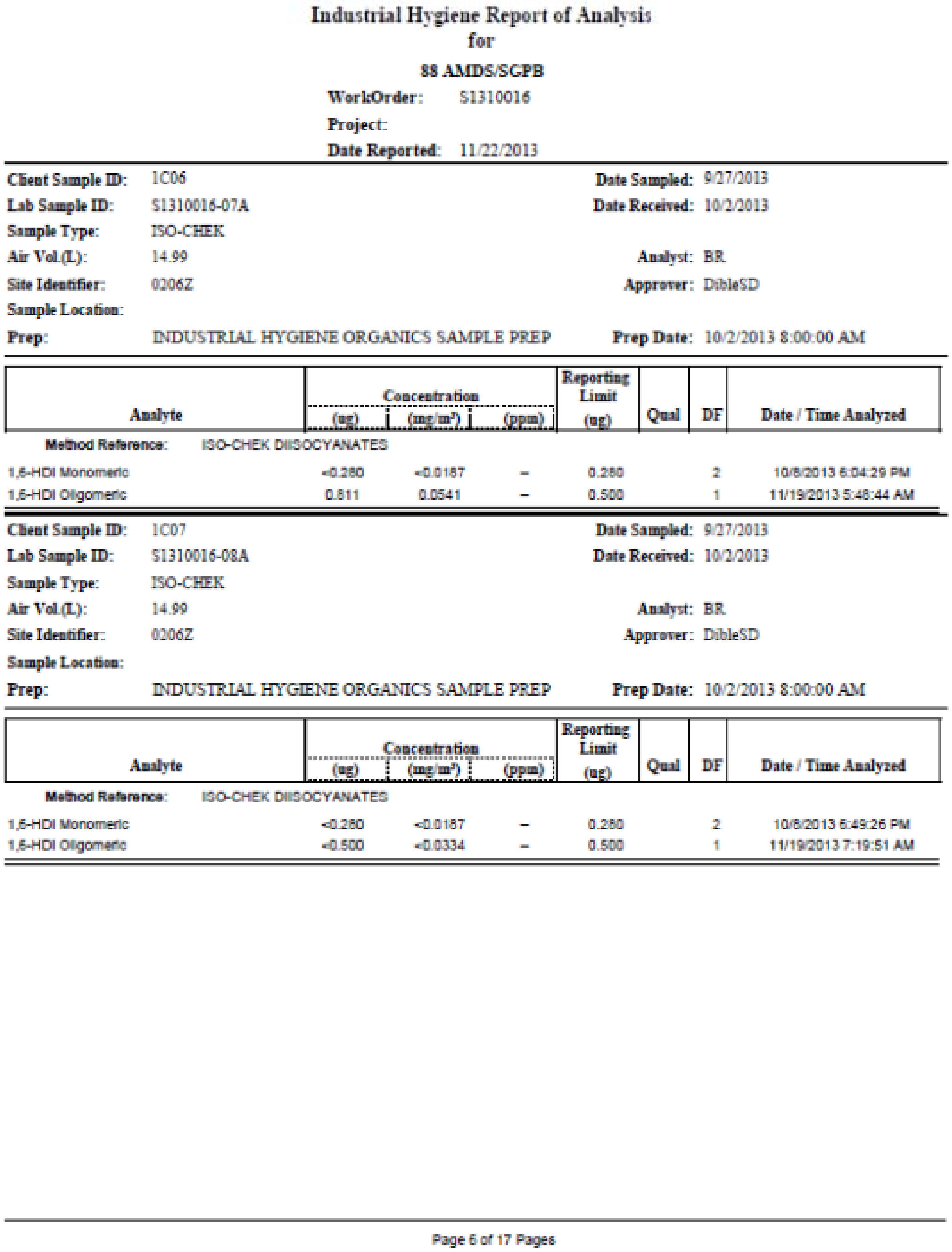

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310016

Project:

Date Reported: 11/22/2013

Client Sample ID:	1C06	**Date Sampled:**	9/27/2013
Lab Sample ID:	S1310016-07A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	14.99	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:			
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	Concentration (mg/m^3)	Concentration (ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0187	–	0.280		2	10/8/2013 6:04:29 PM
1,6-HDI Oligomeric	0.811	0.0541	–	0.500		1	11/19/2013 5:48:44 AM

Client Sample ID:	1C07	**Date Sampled:**	9/27/2013
Lab Sample ID:	S1310016-08A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	14.99	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:			
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	Concentration (mg/m^3)	Concentration (ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0187	–	0.280		2	10/8/2013 6:49:26 PM
1,6-HDI Oligomeric	<0.500	<0.0334	–	0.500		1	11/19/2013 7:19:51 AM

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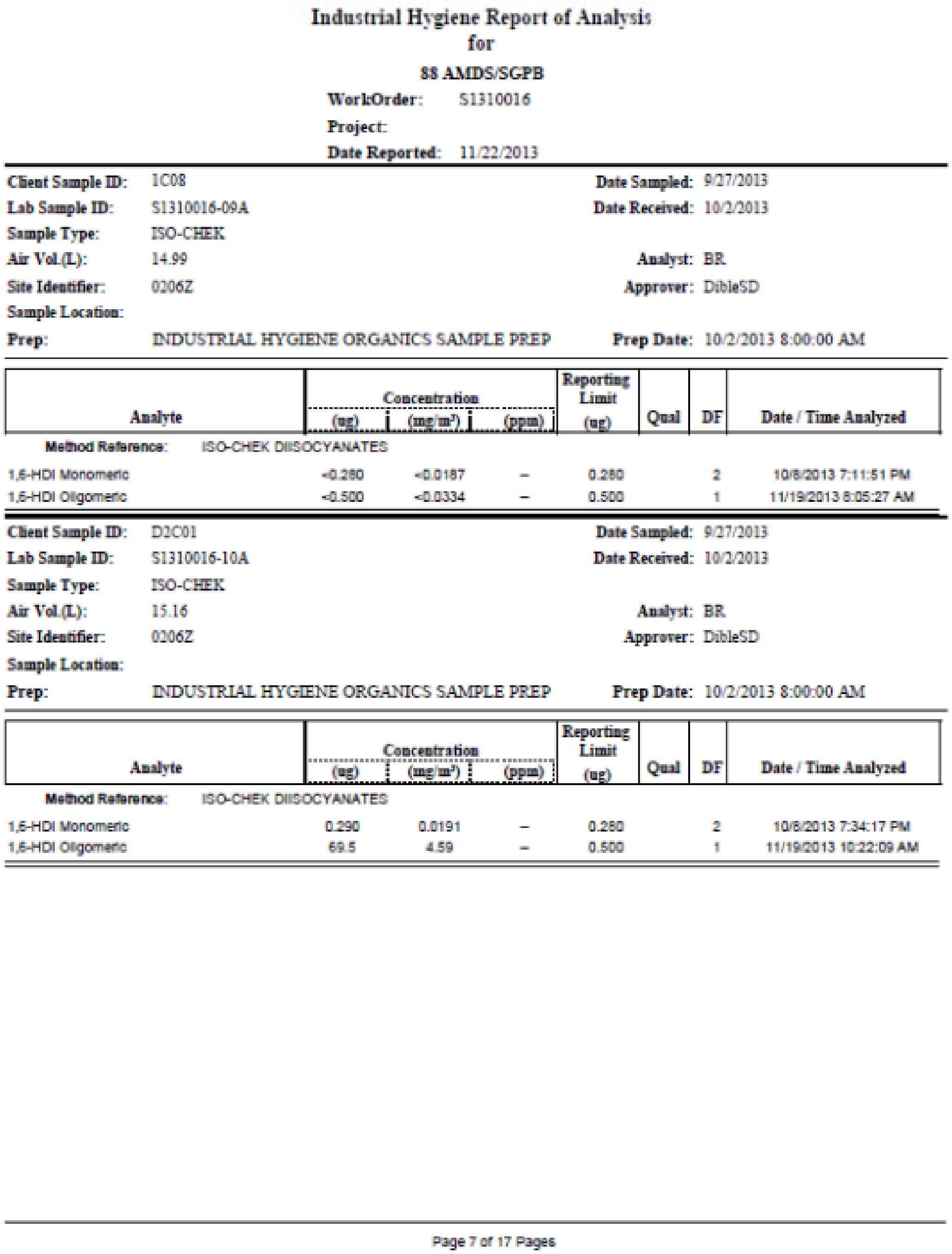

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310016
Project:
Date Reported: 11/22/2013

Client Sample ID:	1C08	**Date Sampled:**	9/27/2013
Lab Sample ID:	S1310016-09A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	14.99	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:			
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m^3)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0187	--	0.280		2	10/8/2013 7:11:51 PM
1,6-HDI Oligomeric	<0.500	<0.0334	--	0.500		1	11/19/2013 8:05:27 AM

Client Sample ID:	D2C01	**Date Sampled:**	9/27/2013
Lab Sample ID:	S1310016-10A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	15.16	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:			
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m^3)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	0.290	0.0191	--	0.280		2	10/8/2013 7:34:17 PM
1,6-HDI Oligomeric	69.5	4.59	--	0.500		1	11/19/2013 10:22:09 AM

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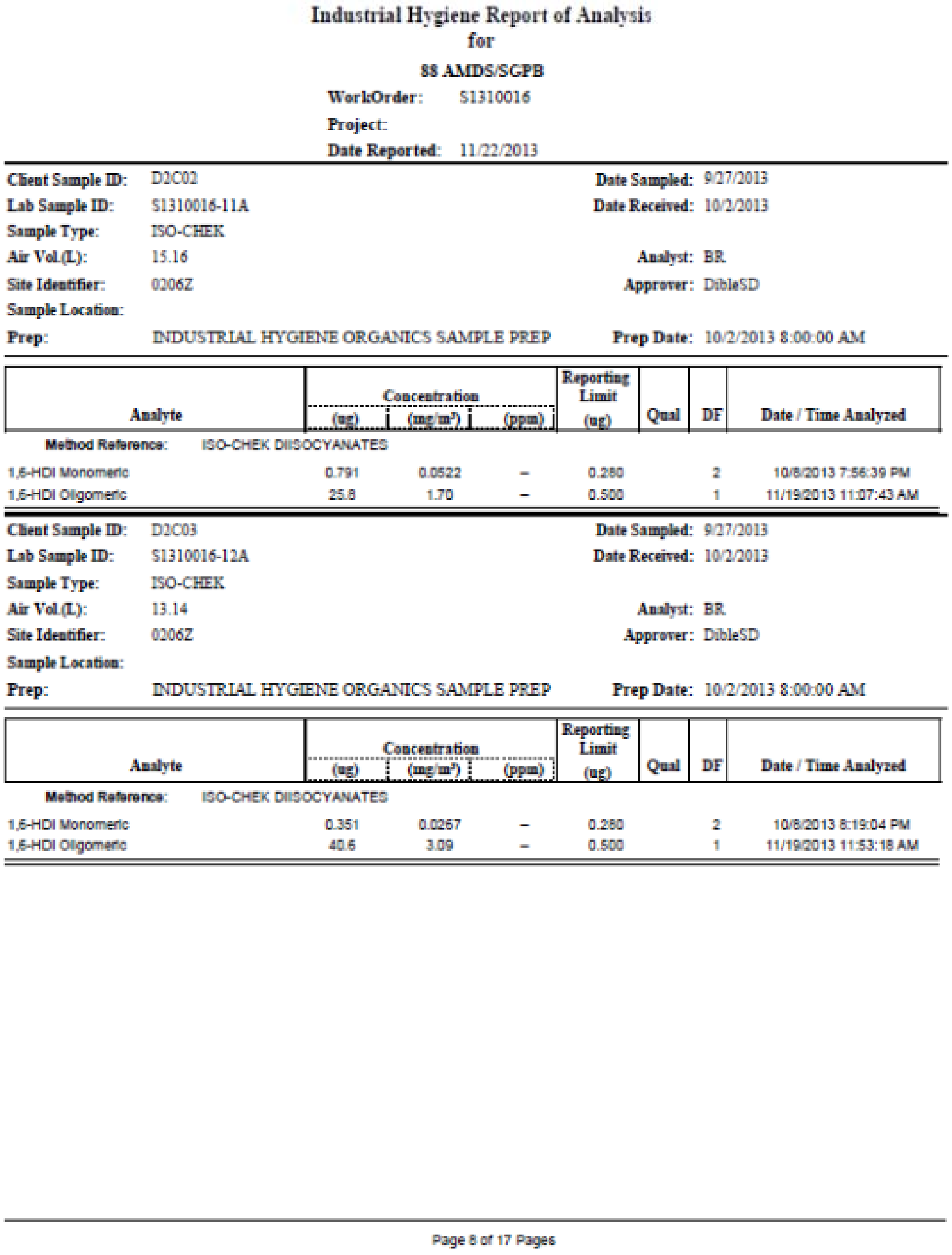

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310016
Project:
Date Reported: 11/22/2013

Client Sample ID:	D2C02	**Date Sampled:**	9/27/2013
Lab Sample ID:	S1310016-11A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	15.16	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:			
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	**Concentration**			**Reporting Limit**	**Qual**	**DF**	**Date / Time Analyzed**
	(ug)	**(mg/m³)**	**(ppm)**	**(ug)**			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	0.791	0.0522	--	0.260		2	10/8/2013 7:56:39 PM
1,6-HDI Oligomeric	25.8	1.70	--	0.500		1	11/19/2013 11:07:43 AM

Client Sample ID:	D2C03	**Date Sampled:**	9/27/2013
Lab Sample ID:	S1310016-12A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	13.14	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:			
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	**Concentration**			**Reporting Limit**	**Qual**	**DF**	**Date / Time Analyzed**
	(ug)	**(mg/m³)**	**(ppm)**	**(ug)**			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	0.351	0.0267	--	0.260		2	10/8/2013 8:19:04 PM
1,6-HDI Oligomeric	40.6	3.09	--	0.500		1	11/19/2013 11:53:18 AM

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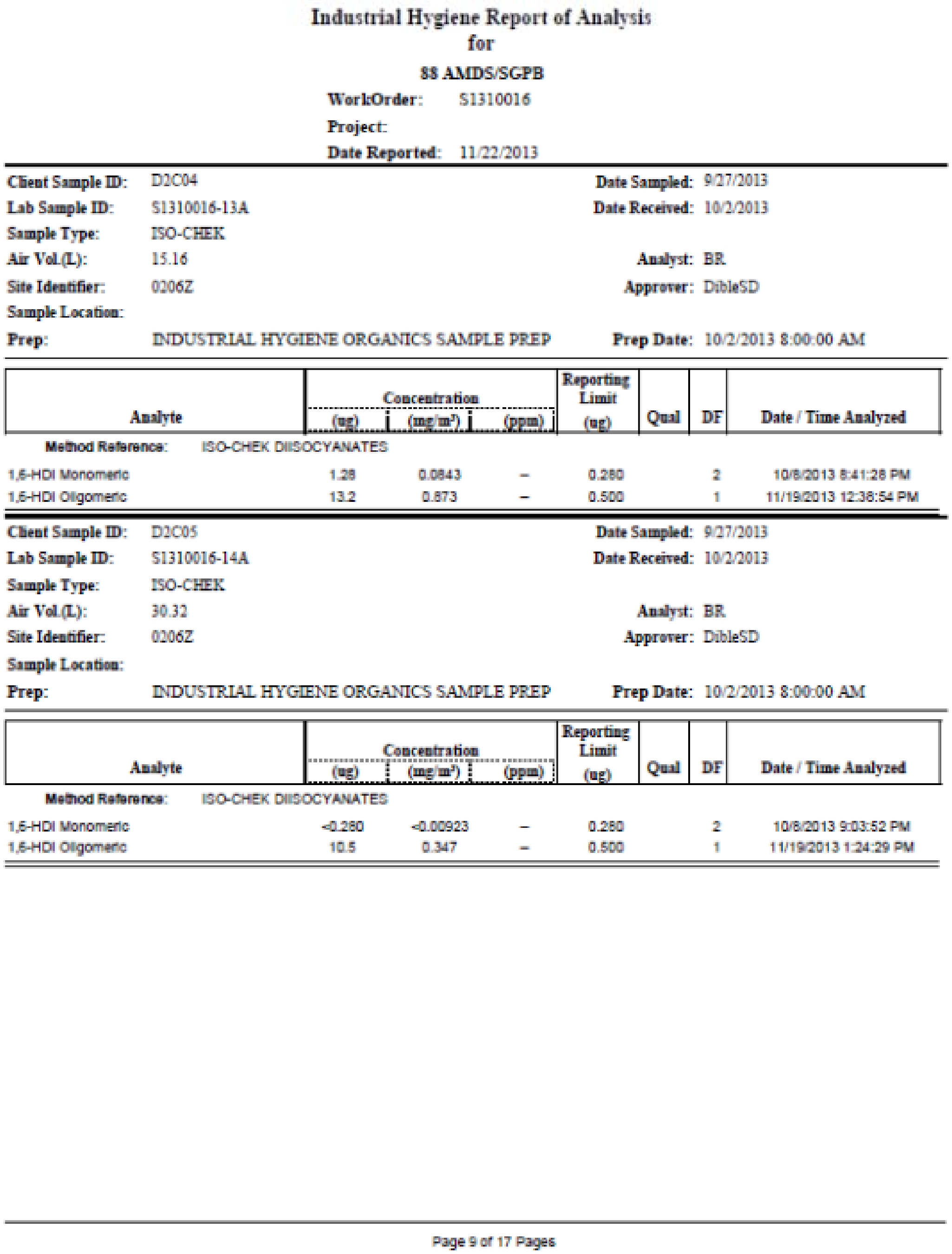

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310016
Project:
Date Reported: 11/22/2013

Client Sample ID: D2C04 **Date Sampled:** 9/27/2013
Lab Sample ID: S1310016-13A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 15.16 **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location:
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m^3)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	1.28	0.0843	--	0.280		2	10/8/2013 8:41:28 PM
1,6-HDI Oligomeric	13.2	0.873	--	0.500		1	11/19/2013 12:38:54 PM

Client Sample ID: D2C05 **Date Sampled:** 9/27/2013
Lab Sample ID: S1310016-14A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 30.32 **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location:
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m^3)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.00923	--	0.280		2	10/8/2013 9:03:52 PM
1,6-HDI Oligomeric	10.5	0.347	--	0.500		1	11/19/2013 1:24:29 PM

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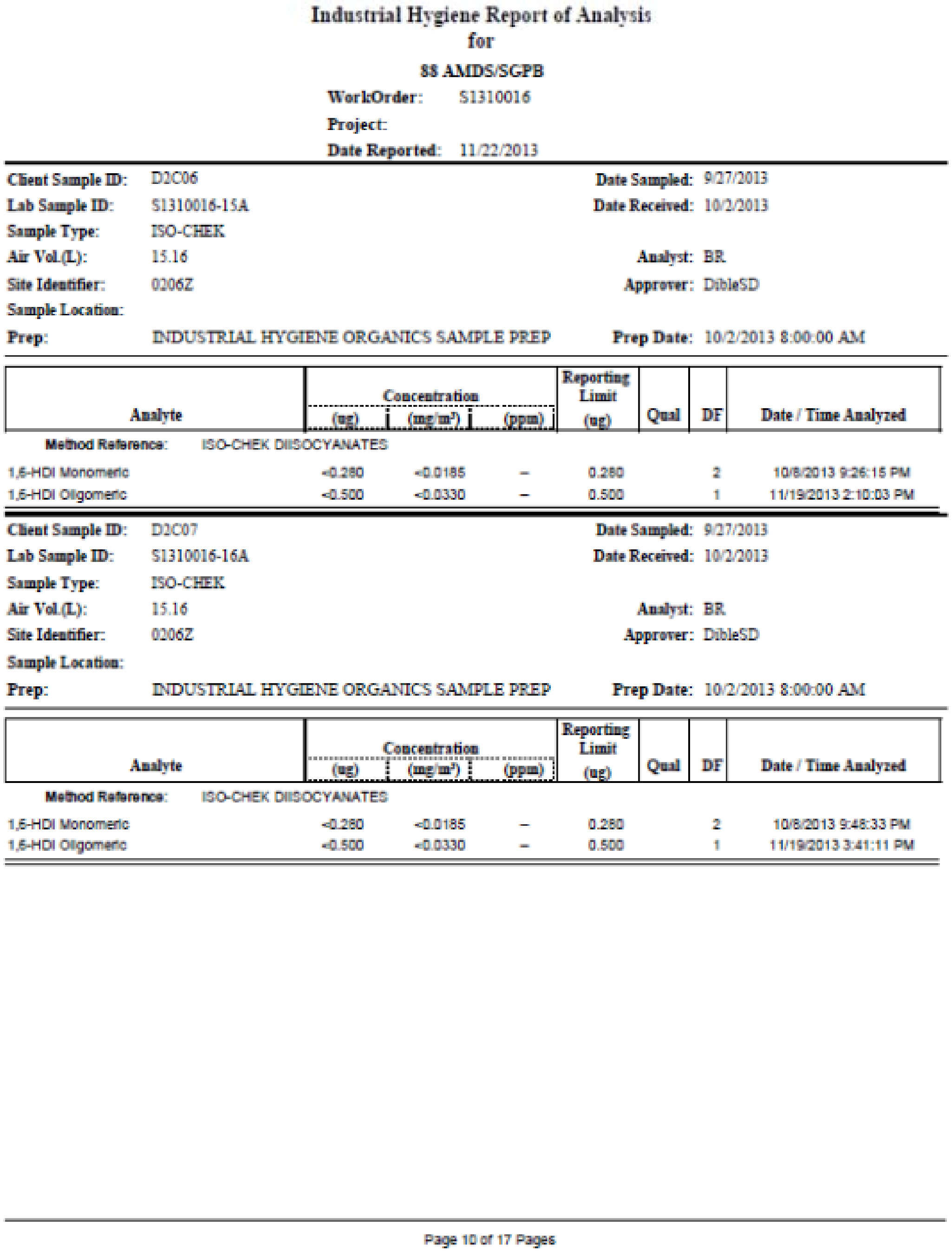

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310016

Project:

Date Reported: 11/22/2013

Client Sample ID: D2C06
Date Sampled: 9/27/2013
Lab Sample ID: S1310016-15A
Date Received: 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 15.16
Analyst: BR
Site Identifier: 0206Z
Approver: DibleSD
Sample Location:
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP
Prep Date: 10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	Concentration (mg/m³)	Concentration (ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0185	–	0.280		2	10/8/2013 9:26:15 PM
1,6-HDI Oligomeric	<0.500	<0.0330	–	0.500		1	11/19/2013 2:10:03 PM

Client Sample ID: D2C07
Date Sampled: 9/27/2013
Lab Sample ID: S1310016-16A
Date Received: 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 15.16
Analyst: BR
Site Identifier: 0206Z
Approver: DibleSD
Sample Location:
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP
Prep Date: 10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	Concentration (mg/m³)	Concentration (ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0185	–	0.280		2	10/8/2013 9:48:33 PM
1,6-HDI Oligomeric	<0.500	<0.0330	–	0.500		1	11/19/2013 3:41:11 PM

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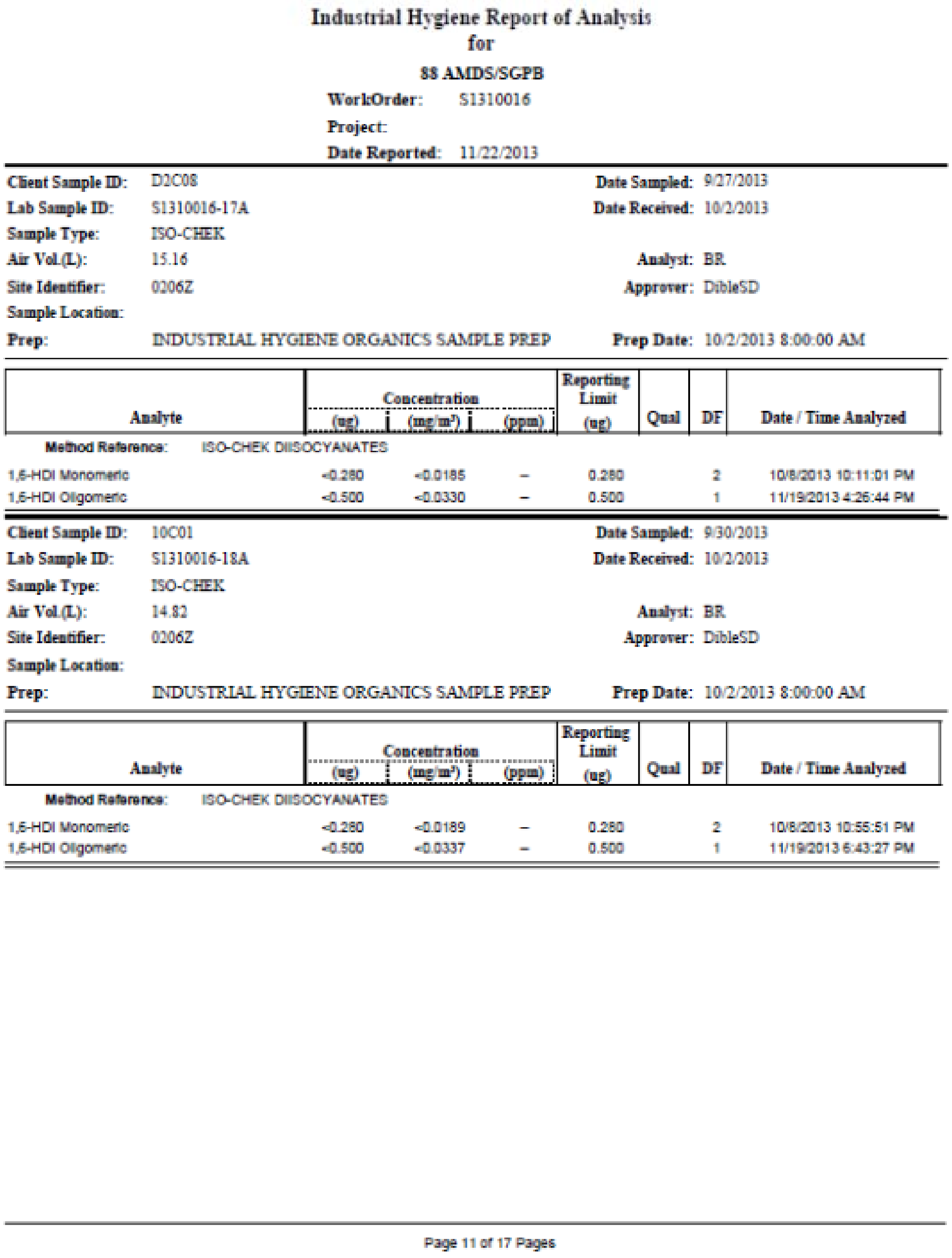

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310016
Project:
Date Reported: 11/22/2013

Client Sample ID:	D2C08	**Date Sampled:**	9/27/2013
Lab Sample ID:	S1310016-17A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	15.16	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:			
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m³)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0185	–	0.280		2	10/8/2013 10:11:01 PM
1,6-HDI Oligomeric	<0.500	<0.0330	–	0.500		1	11/19/2013 4:26:44 PM

Client Sample ID:	10C01	**Date Sampled:**	9/30/2013
Lab Sample ID:	S1310016-18A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	14.82	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:			
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m³)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0189	–	0.280		2	10/8/2013 10:55:51 PM
1,6-HDI Oligomeric	<0.500	<0.0337	–	0.500		1	11/19/2013 6:43:27 PM

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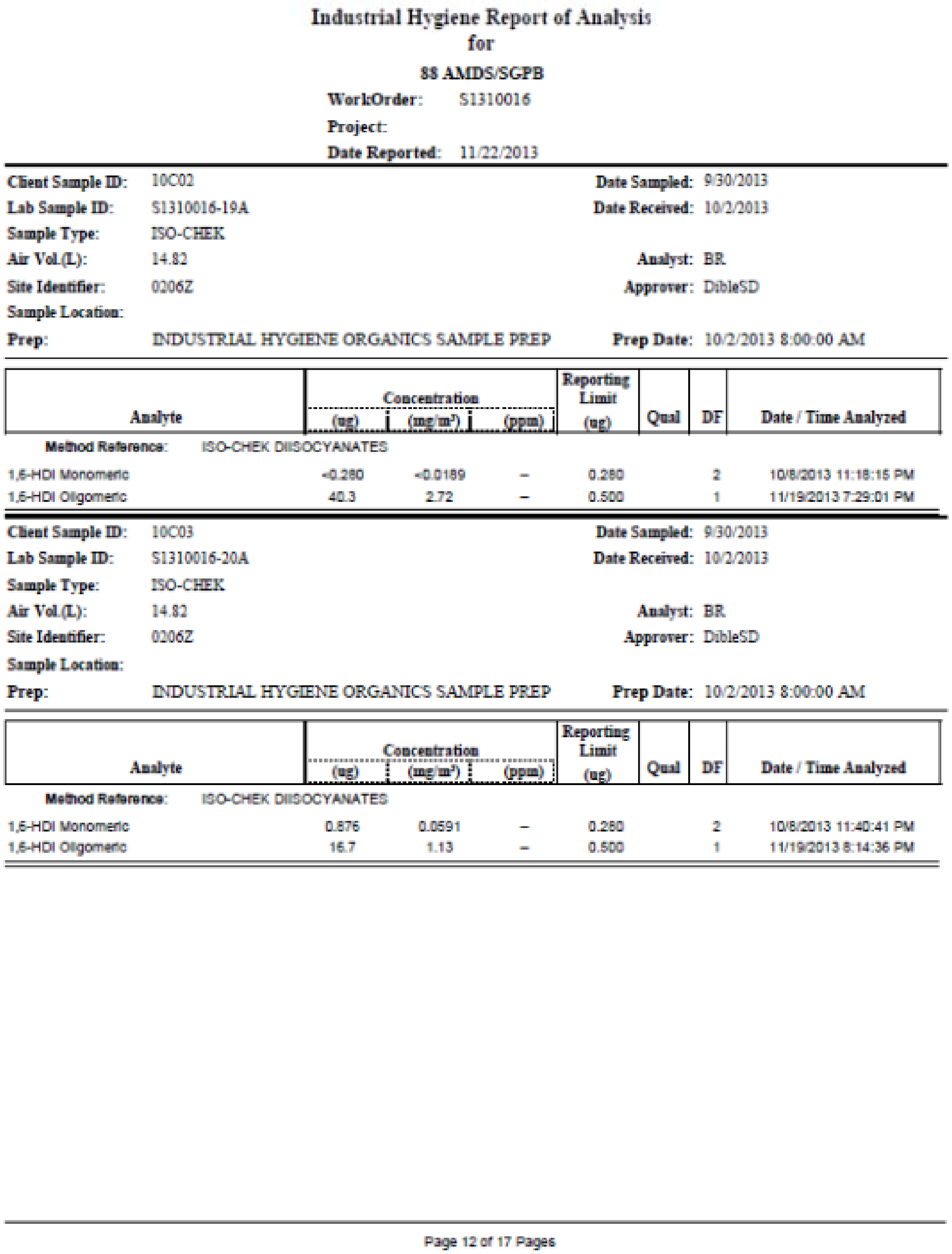

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310016
Project:
Date Reported: 11/22/2013

Client Sample ID: 10C02 **Date Sampled:** 9/30/2013
Lab Sample ID: S1310016-19A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 14.82 **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location:
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m³)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0189	--	0.280		2	10/8/2013 11:18:15 PM
1,6-HDI Oligomeric	40.3	2.72	--	0.500		1	11/19/2013 7:29:01 PM

Client Sample ID: 10C03 **Date Sampled:** 9/30/2013
Lab Sample ID: S1310016-20A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 14.82 **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location:
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m³)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	0.876	0.0591	--	0.280		2	10/8/2013 11:40:41 PM
1,6-HDI Oligomeric	16.7	1.13	--	0.500		1	11/19/2013 8:14:36 PM

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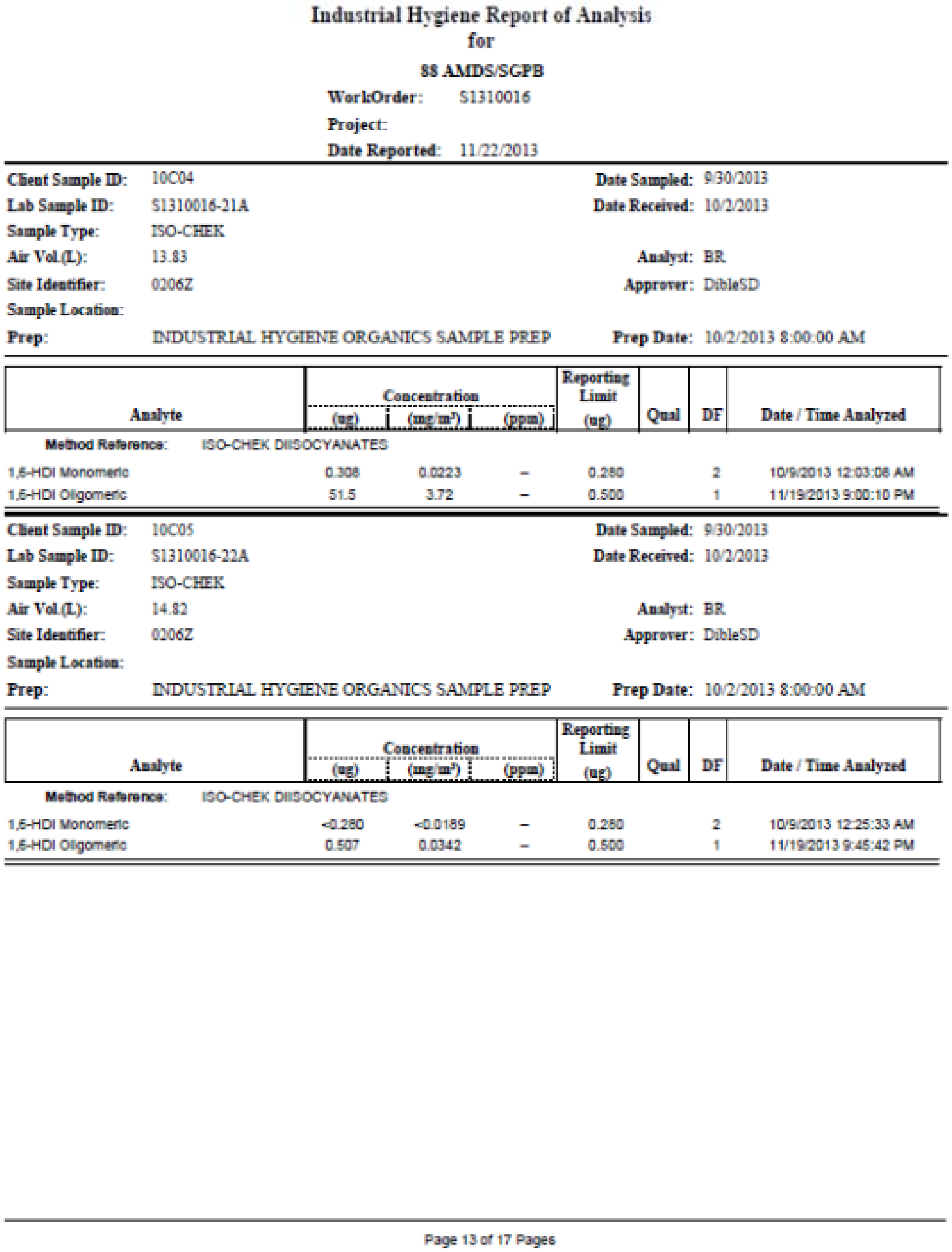

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310016
Project:
Date Reported: 11/22/2013

Client Sample ID:	10C04	**Date Sampled:**	9/30/2013
Lab Sample ID:	S1310016-21A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	13.83	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:			
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	Concentration (mg/m³)	Concentration (ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	0.308	0.0223	--	0.260		2	10/9/2013 12:03:08 AM
1,6-HDI Oligomeric	51.5	3.72	--	0.500		1	11/19/2013 9:00:10 PM

Client Sample ID:	10C05	**Date Sampled:**	9/30/2013
Lab Sample ID:	S1310016-22A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	14.82	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:			
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	Concentration (mg/m³)	Concentration (ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.260	<0.0189	--	0.260		2	10/9/2013 12:25:33 AM
1,6-HDI Oligomeric	0.507	0.0342	--	0.500		1	11/19/2013 9:45:42 PM

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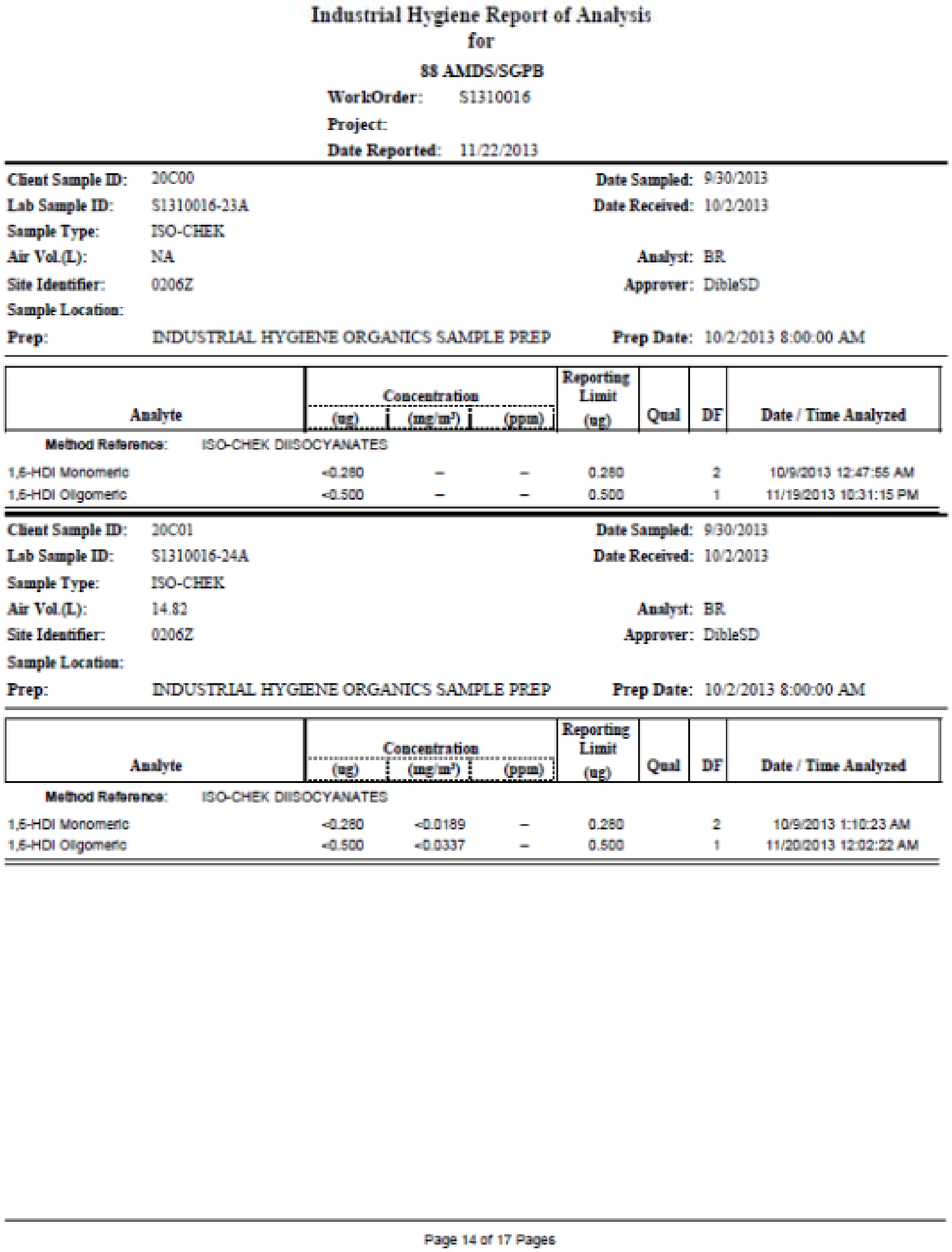


Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310016

Project:

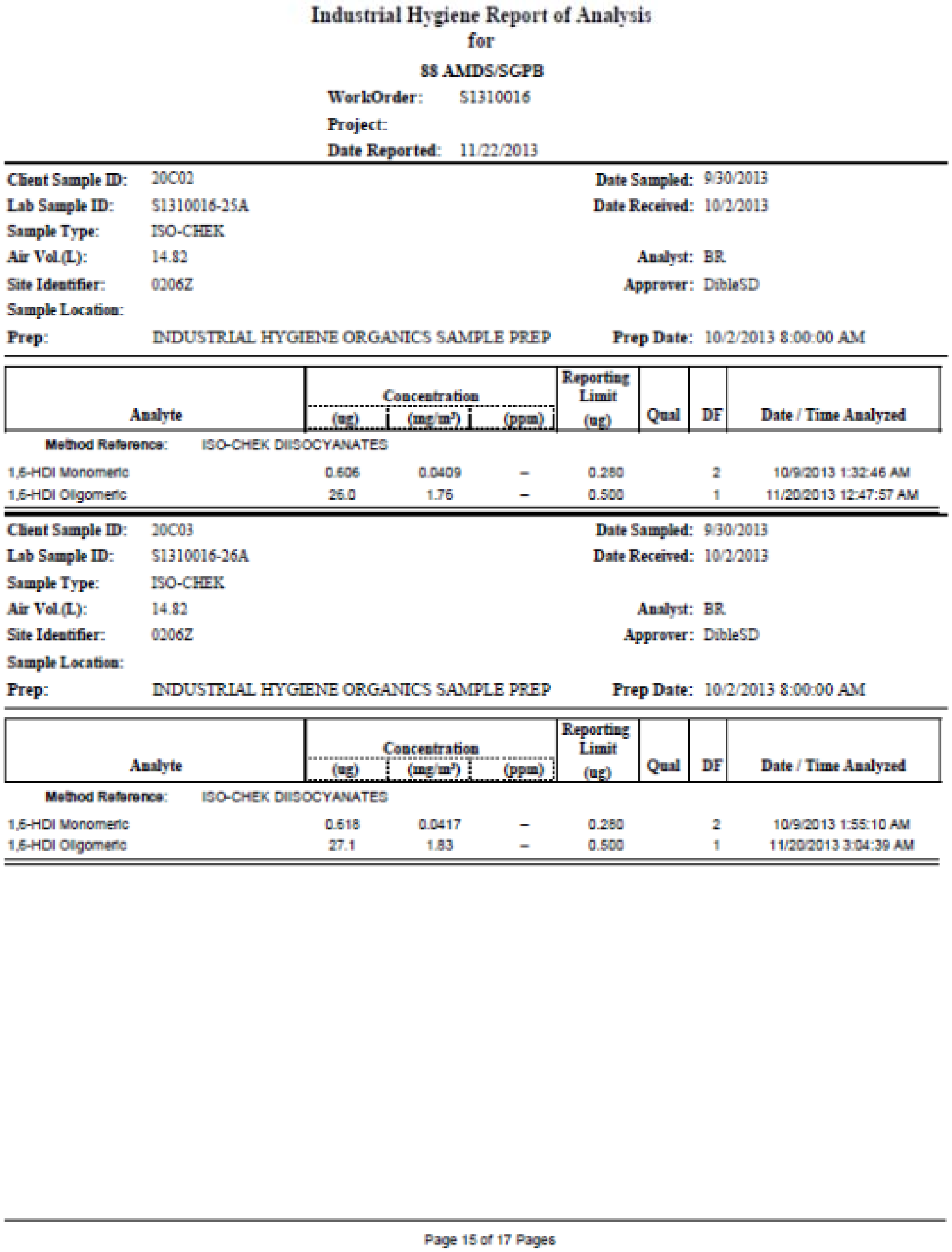
Date Reported: 11/22/2013

Client Sample ID:	20C00	**Date Sampled:**	9/30/2013
Lab Sample ID:	S1310016-23A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	NA	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:			
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m³)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	–	–	0.280		2	10/9/2013 12:47:55 AM
1,6-HDI Oligomeric	<0.500	–	–	0.500		1	11/19/2013 10:31:15 PM

Client Sample ID:	20C01	**Date Sampled:**	9/30/2013
Lab Sample ID:	S1310016-24A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	14.82	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:			
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m³)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0189	–	0.280		2	10/9/2013 1:10:23 AM
1,6-HDI Oligomeric	<0.500	<0.0337	–	0.500		1	11/20/2013 12:02:22 AM



Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310016
Project:
Date Reported: 11/22/2013

Client Sample ID:	20C02	**Date Sampled:**	9/30/2013
Lab Sample ID:	S1310016-25A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	14.82	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:			
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m^3)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	0.606	0.0409	--	0.260		2	10/9/2013 1:32:46 AM
1,6-HDI Oligomeric	26.0	1.76	--	0.500		1	11/20/2013 12:47:57 AM

Client Sample ID:	20C03	**Date Sampled:**	9/30/2013
Lab Sample ID:	S1310016-26A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	14.82	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:			
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m^3)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	0.618	0.0417	--	0.260		2	10/9/2013 1:55:10 AM
1,6-HDI Oligomeric	27.1	1.83	--	0.500		1	11/20/2013 3:04:39 AM

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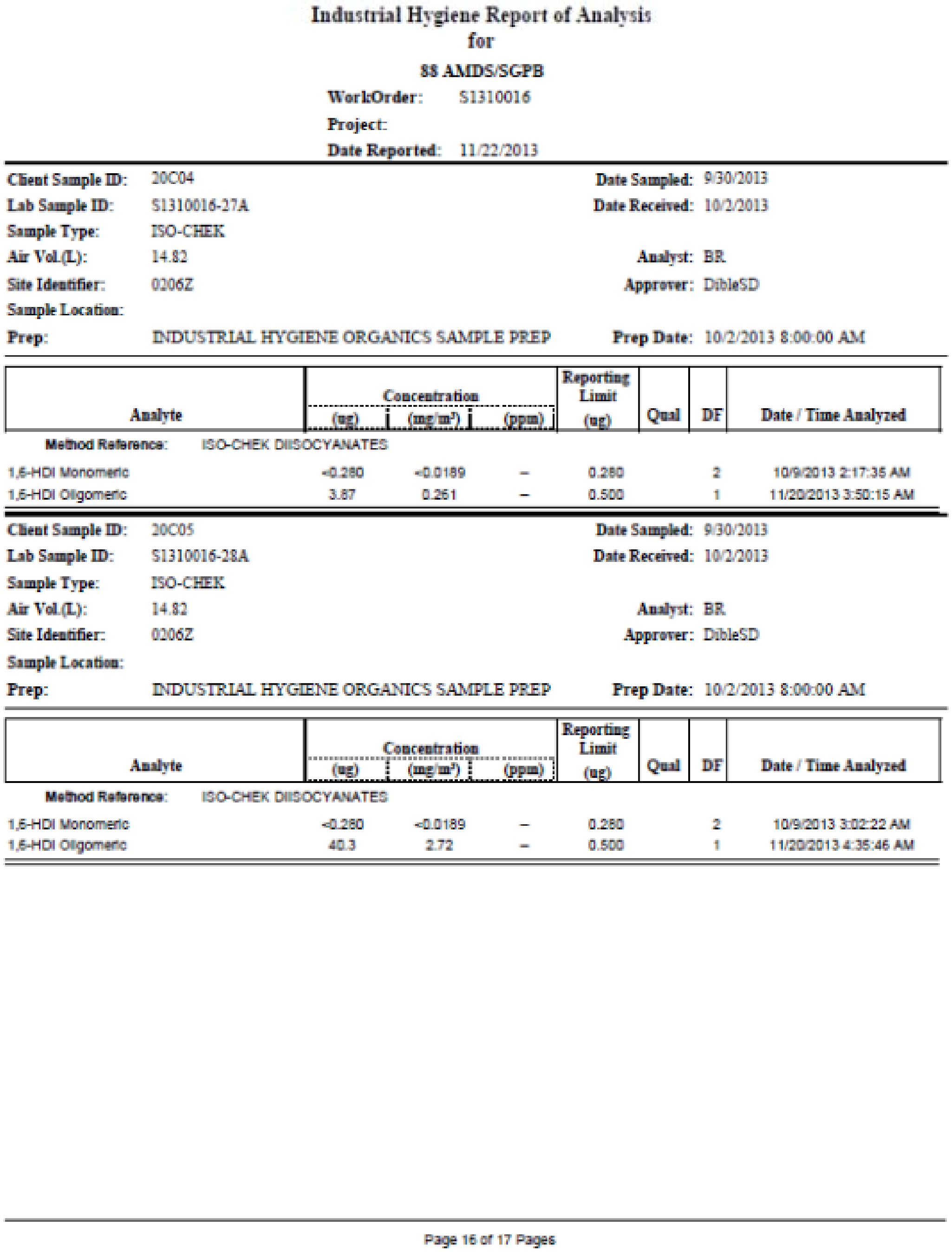

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310016

Project:

Date Reported: 11/22/2013

Client Sample ID:	20C04	**Date Sampled:**	9/30/2013
Lab Sample ID:	S1310016-27A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	14.82	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:			
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	(mg/m³)	(ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0189	--	0.280		2	10/9/2013 2:17:36 AM
1,6-HDI Oligomeric	3.87	0.261	--	0.500		1	11/20/2013 3:50:15 AM

Client Sample ID:	20C05	**Date Sampled:**	9/30/2013
Lab Sample ID:	S1310016-28A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	14.82	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:			
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	(mg/m³)	(ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0189	--	0.280		2	10/9/2013 3:02:22 AM
1,6-HDI Oligomeric	40.3	2.72	--	0.500		1	11/20/2013 4:35:46 AM

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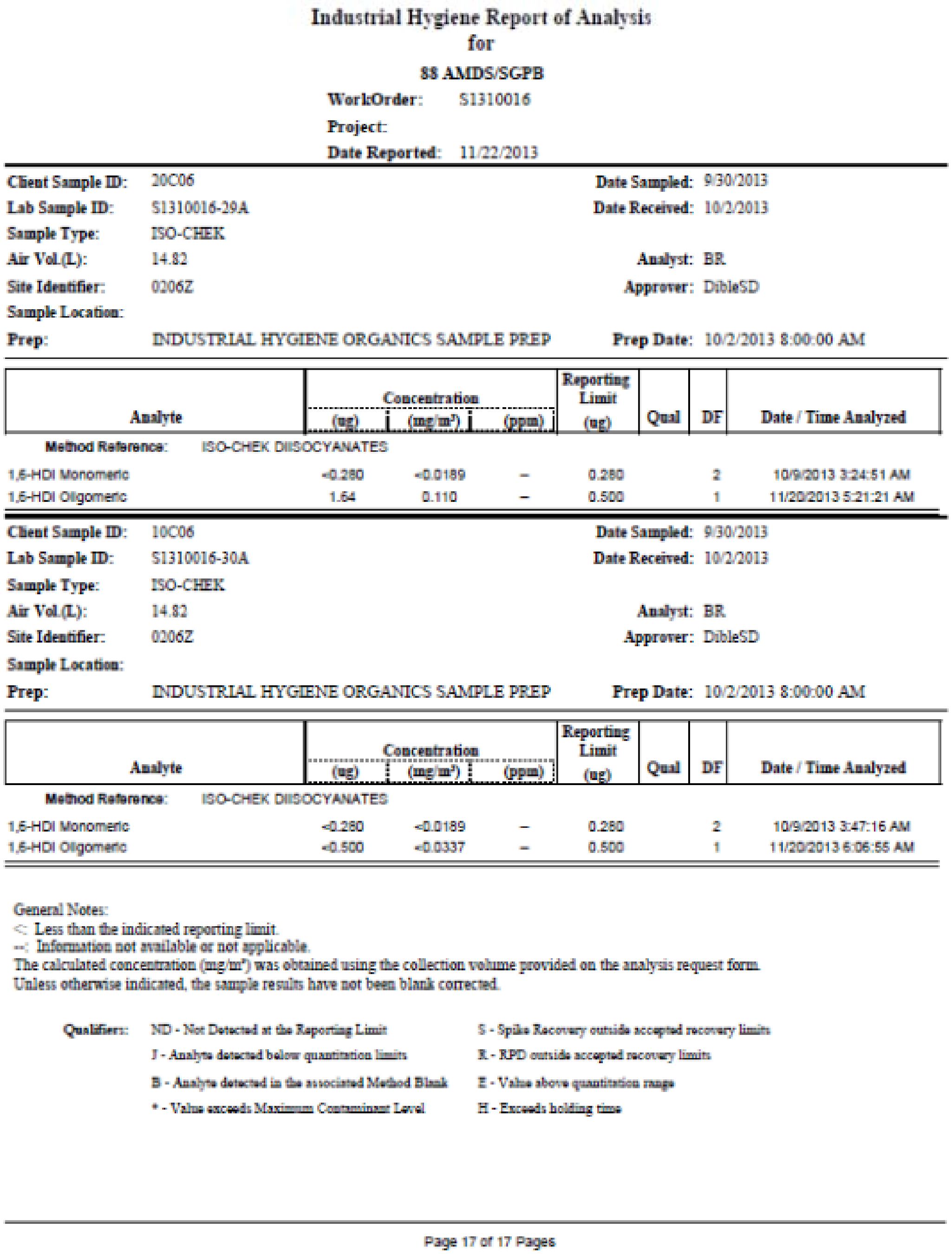

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310016
Project:
Date Reported: 11/22/2013

Client Sample ID: 20C06
Lab Sample ID: S1310016-29A
Sample Type: ISO-CHEK
Air Vol.(L): 14.82
Site Identifier: 0206Z
Sample Location:
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP

Date Sampled: 9/30/2013
Date Received: 10/2/2013
Analyst: BR
Approver: DibleSD
Prep Date: 10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	Concentration (mg/m³)	Concentration (ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0189	--	0.280		2	10/9/2013 3:24:51 AM
1,6-HDI Oligomeric	1.64	0.110	--	0.500		1	11/20/2013 5:21:21 AM

Client Sample ID: 10C06
Lab Sample ID: S1310016-30A
Sample Type: ISO-CHEK
Air Vol.(L): 14.82
Site Identifier: 0206Z
Sample Location:
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP

Date Sampled: 9/30/2013
Date Received: 10/2/2013
Analyst: BR
Approver: DibleSD
Prep Date: 10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	Concentration (mg/m³)	Concentration (ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0189	--	0.280		2	10/9/2013 3:47:16 AM
1,6-HDI Oligomeric	<0.500	<0.0337	--	0.500		1	11/20/2013 6:06:55 AM

General Notes:
<: Less than the indicated reporting limit.
--: Information not available or not applicable.
The calculated concentration (mg/m³) was obtained using the collection volume provided on the analysis request form.
Unless otherwise indicated, the sample results have not been blank corrected.

Qualifiers:

ND - Not Detected at the Reporting Limit	S - Spike Recovery outside accepted recovery limits
J - Analyte detected below quantitation limits	R - RPD outside accepted recovery limits
B - Analyte detected in the associated Method Blank	E - Value above quantitation range
* - Value exceeds Maximum Contaminant Level	H - Exceeds holding time

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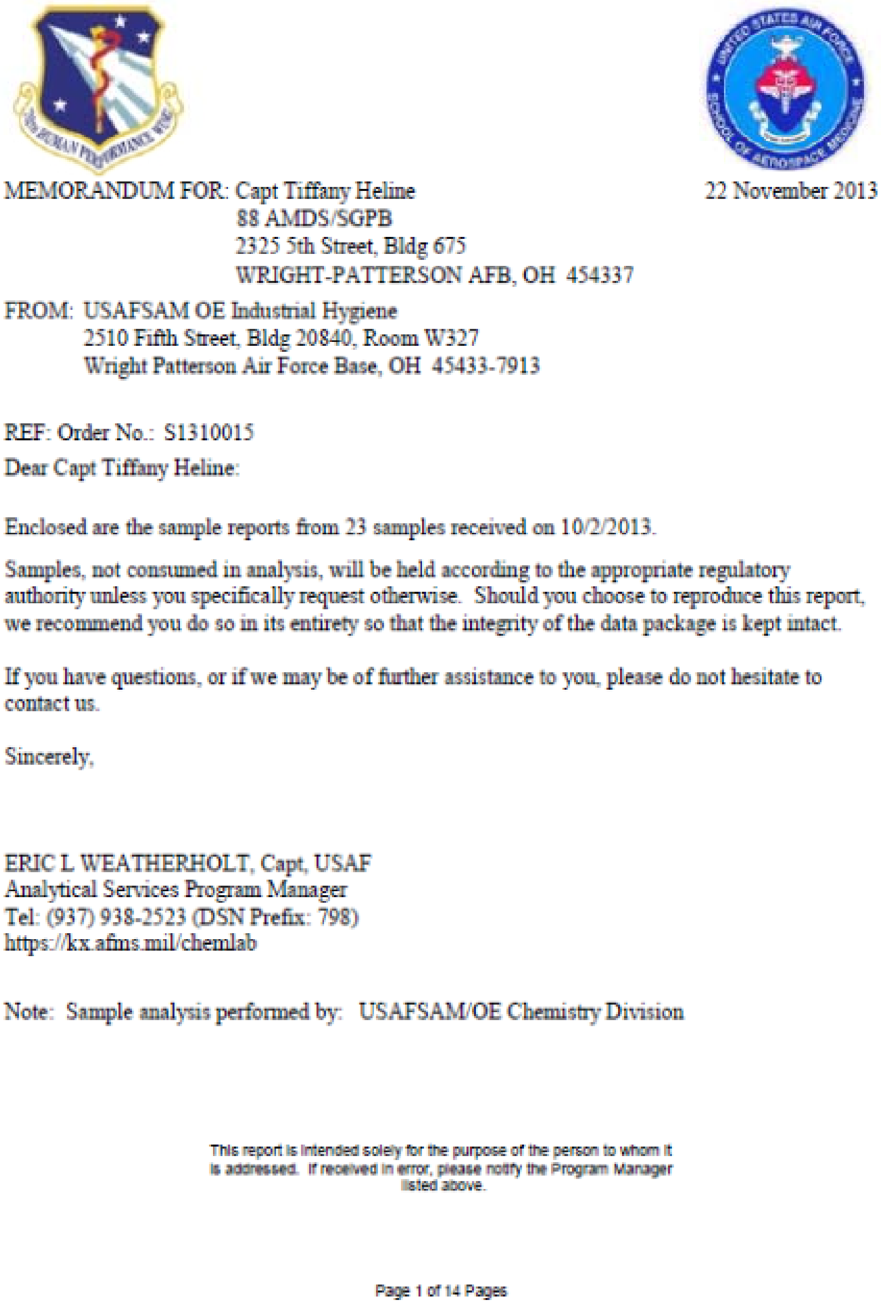


MEMORANDUM FOR: Capt Tiffany Heline
88 AMDS/SGPB
2325 5th Street, Bldg 675
WRIGHT-PATTERSON AFB, OH 454337

22 November 2013

FROM: USAFSAM OE Industrial Hygiene
2510 Fifth Street, Bldg 20840, Room W327
Wright Patterson Air Force Base, OH 45433-7913

REF: Order No.: S1310015

Dear Capt Tiffany Heline:

Enclosed are the sample reports from 23 samples received on 10/2/2013.

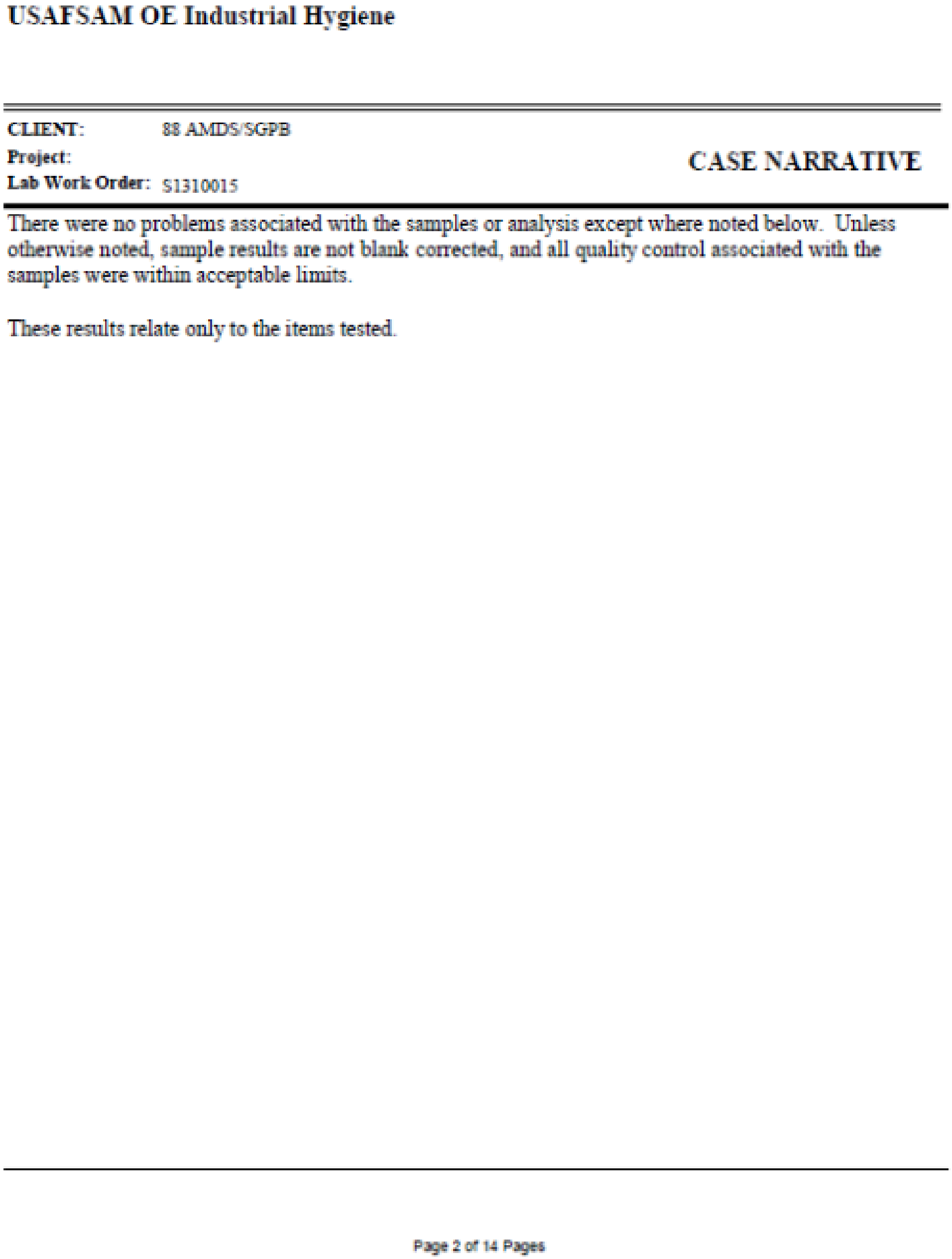
Samples, not consumed in analysis, will be held according to the appropriate regulatory authority unless you specifically request otherwise. Should you choose to reproduce this report, we recommend you do so in its entirety so that the integrity of the data package is kept intact.

If you have questions, or if we may be of further assistance to you, please do not hesitate to contact us.

Sincerely,

ERIC L WEATHERHOLT, Capt, USAF
Analytical Services Program Manager
Tel: (937) 938-2523 (DSN Prefix: 798)
https://kx.afms.mil/chemlab

Note: Sample analysis performed by: USAFSAM/OE Chemistry Division

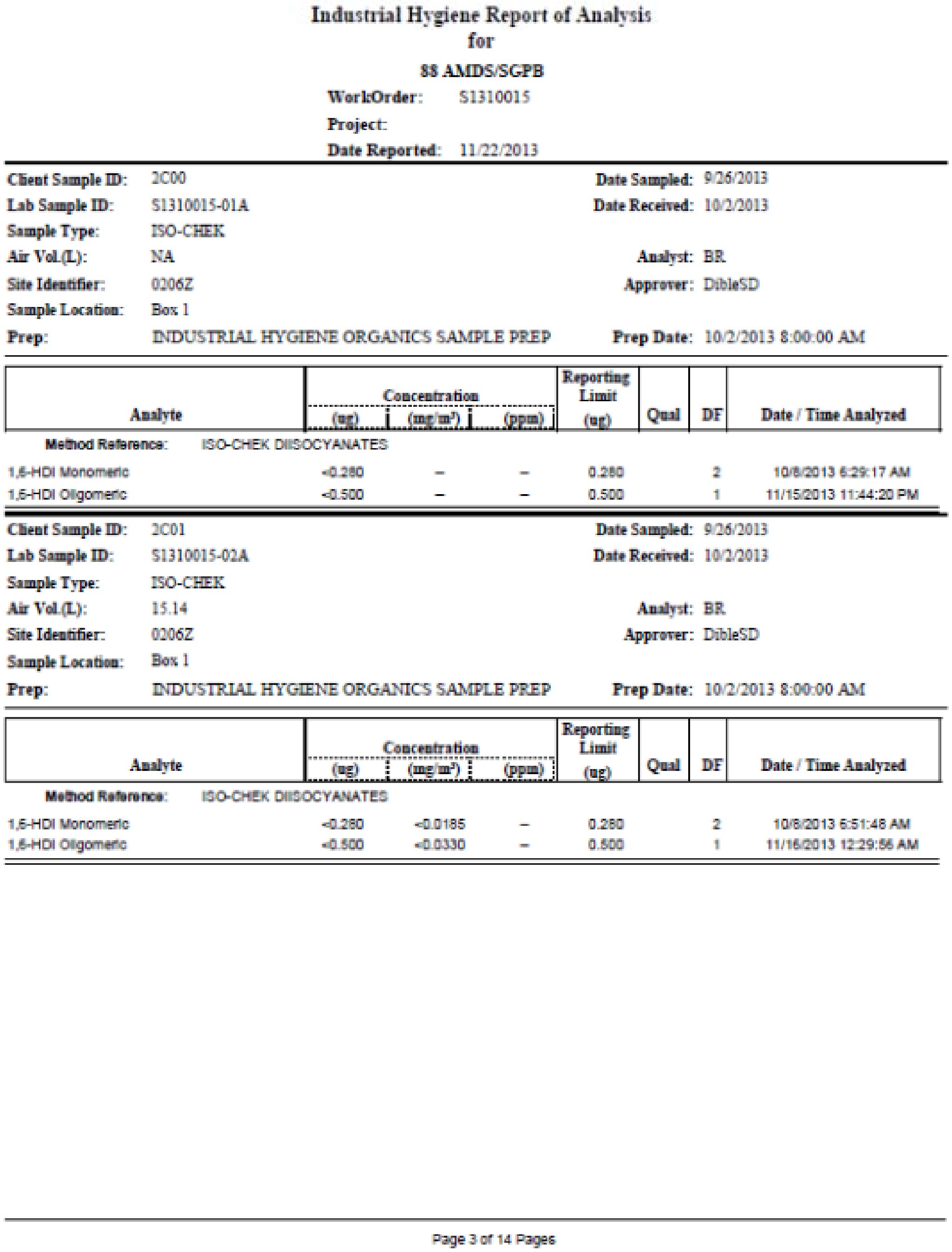


USAFSAM OE Industrial Hygiene

CLIENT:	88 AMDS/SGPB	**CASE NARRATIVE**
Project:		
Lab Work Order:	S1310015	

There were no problems associated with the samples or analysis except where noted below. Unless otherwise noted, sample results are not blank corrected, and all quality control associated with the samples were within acceptable limits.

These results relate only to the items tested.



Industrial Hygiene Report of Analysis
for

88 AMDS/SGPB

WorkOrder: S1310015
Project:
Date Reported: 11/22/2013

Client Sample ID: 2C00 **Date Sampled:** 9/26/2013
Lab Sample ID: S1310015-01A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): NA **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location: Box 1
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m³)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	–	–	0.280		2	10/8/2013 6:29:17 AM
1,6-HDI Oligomeric	<0.500	–	–	0.500		1	11/15/2013 11:44:20 PM

Client Sample ID: 2C01 **Date Sampled:** 9/26/2013
Lab Sample ID: S1310015-02A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 15.14 **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location: Box 1
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m³)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0185	–	0.280		2	10/8/2013 6:51:48 AM
1,6-HDI Oligomeric	<0.500	<0.0330	–	0.500		1	11/16/2013 12:29:56 AM

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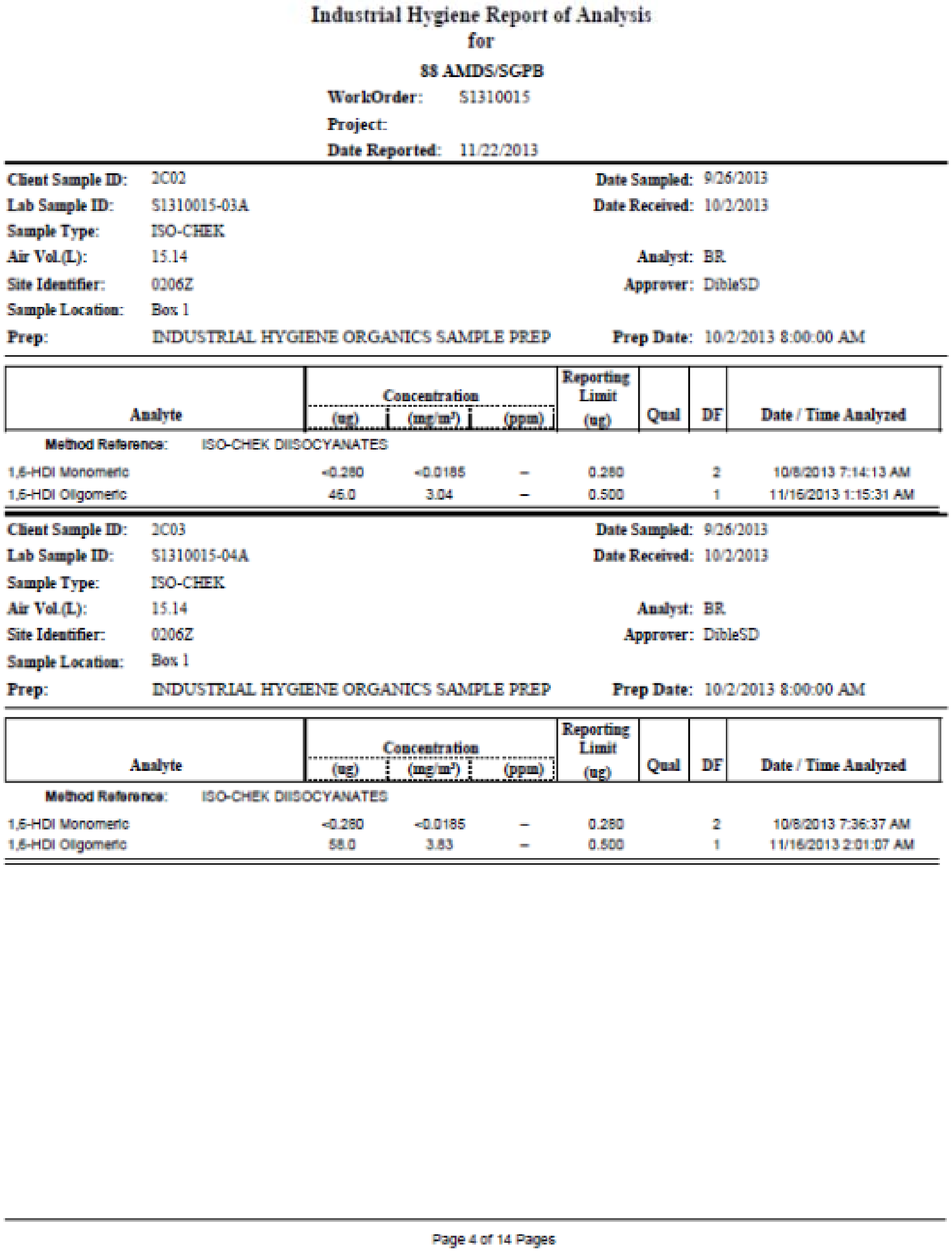

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310015

Project:

Date Reported: 11/22/2013

Client Sample ID: 2C02 **Date Sampled:** 9/26/2013
Lab Sample ID: S1310015-03A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 15.14 **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location: Box 1
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	Concentration (mg/m³)	Concentration (ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0185	--	0.280		2	10/8/2013 7:14:13 AM
1,6-HDI Oligomeric	46.0	3.04	--	0.500		1	11/16/2013 1:15:31 AM

Client Sample ID: 2C03 **Date Sampled:** 9/26/2013
Lab Sample ID: S1310015-04A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 15.14 **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location: Box 1
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	Concentration (mg/m³)	Concentration (ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0185	--	0.280		2	10/8/2013 7:36:37 AM
1,6-HDI Oligomeric	58.0	3.83	--	0.500		1	11/16/2013 2:01:07 AM

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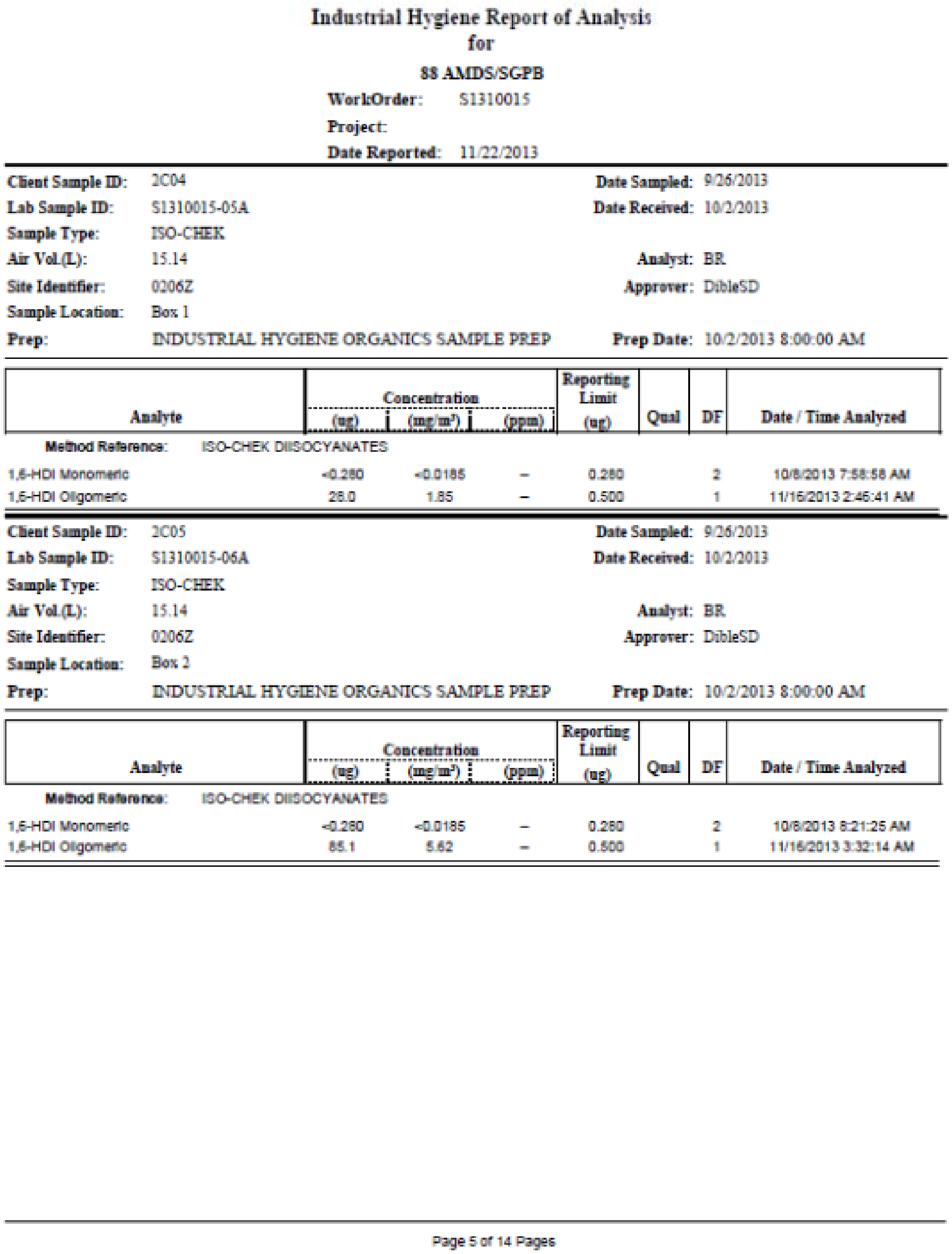

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310015
Project:
Date Reported: 11/22/2013

Client Sample ID: 2C04 **Date Sampled:** 9/26/2013
Lab Sample ID: S1310015-05A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 15.14 **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location: Box 1
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	Concentration (mg/m³)	Concentration (ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0185	--	0.280		2	10/8/2013 7:58:58 AM
1,6-HDI Oligomeric	28.0	1.85	--	0.500		1	11/16/2013 2:46:41 AM

Client Sample ID: 2C05 **Date Sampled:** 9/26/2013
Lab Sample ID: S1310015-06A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 15.14 **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location: Box 2
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	Concentration (mg/m³)	Concentration (ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0185	--	0.280		2	10/8/2013 8:21:25 AM
1,6-HDI Oligomeric	85.1	5.62	--	0.500		1	11/16/2013 3:32:14 AM

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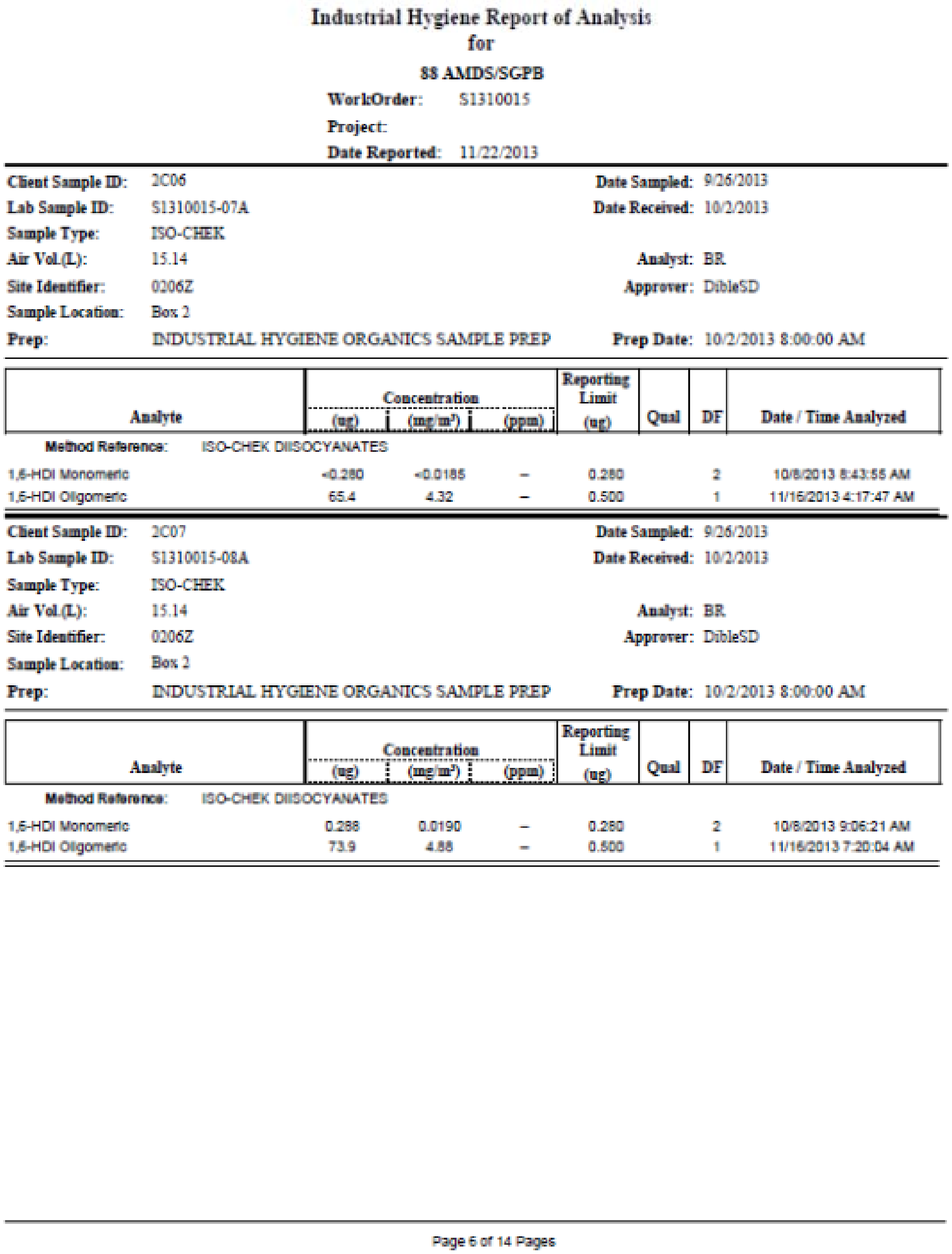

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310015
Project:
Date Reported: 11/22/2013

Client Sample ID: 2C06 **Date Sampled:** 9/26/2013
Lab Sample ID: S1310015-07A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 15.14 **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location: Box 2
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m³)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0185	--	0.280		2	10/8/2013 8:43:55 AM
1,6-HDI Oligomeric	65.4	4.32	--	0.500		1	11/16/2013 4:17:47 AM

Client Sample ID: 2C07 **Date Sampled:** 9/26/2013
Lab Sample ID: S1310015-08A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 15.14 **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location: Box 2
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m³)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	0.288	0.0190	--	0.280		2	10/8/2013 9:06:21 AM
1,6-HDI Oligomeric	73.9	4.88	--	0.500		1	11/16/2013 7:20:04 AM

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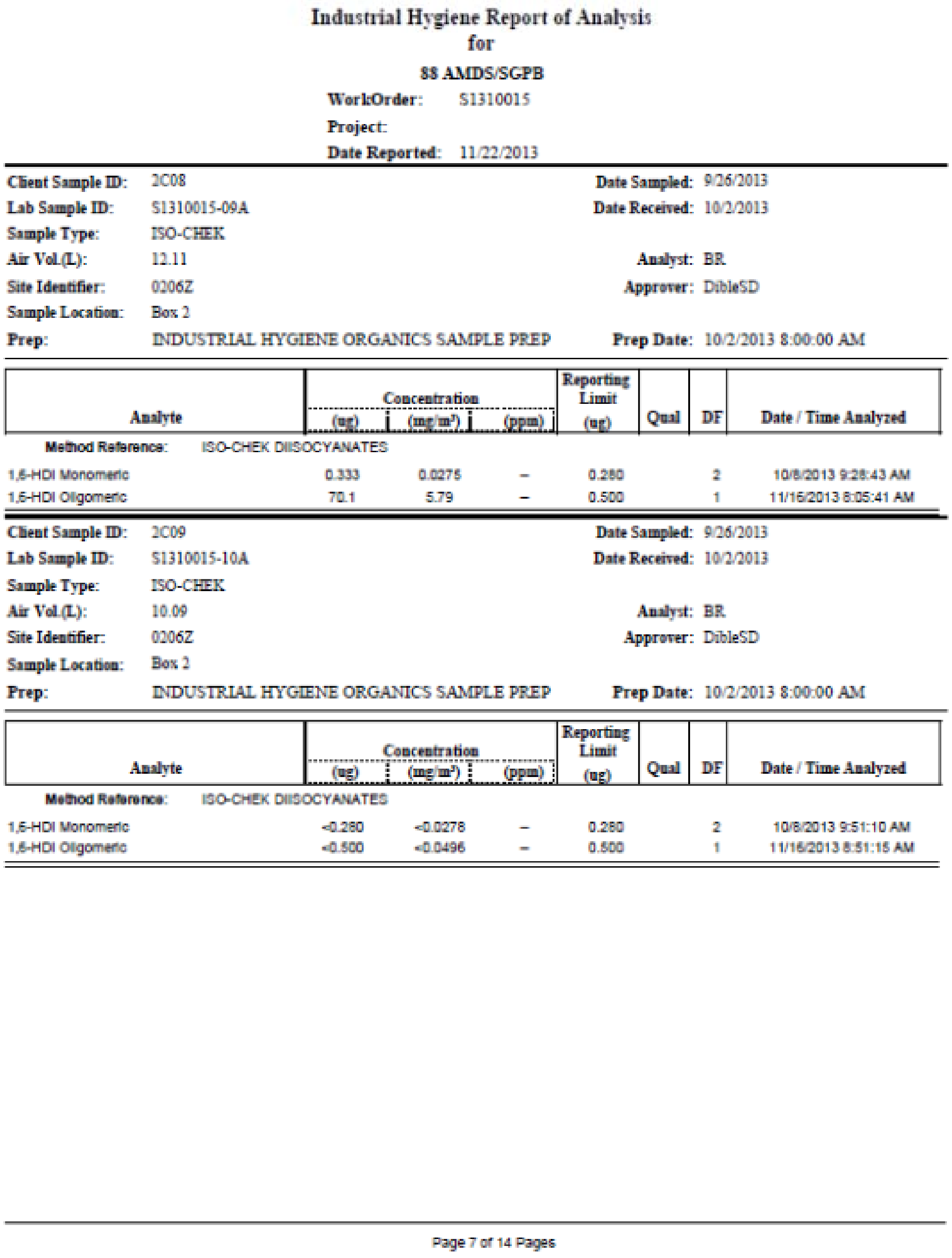

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310015
Project:
Date Reported: 11/22/2013

Client Sample ID: 2C08 **Date Sampled:** 9/26/2013
Lab Sample ID: S1310015-09A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 12.11 **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location: Box 2
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m³)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	0.333	0.0275	--	0.280		2	10/8/2013 9:28:43 AM
1,6-HDI Oligomeric	70.1	5.79	--	0.500		1	11/16/2013 8:05:41 AM

Client Sample ID: 2C09 **Date Sampled:** 9/26/2013
Lab Sample ID: S1310015-10A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 10.09 **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location: Box 2
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m³)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0278	--	0.280		2	10/8/2013 9:51:10 AM
1,6-HDI Oligomeric	<0.500	<0.0496	--	0.500		1	11/16/2013 8:51:15 AM

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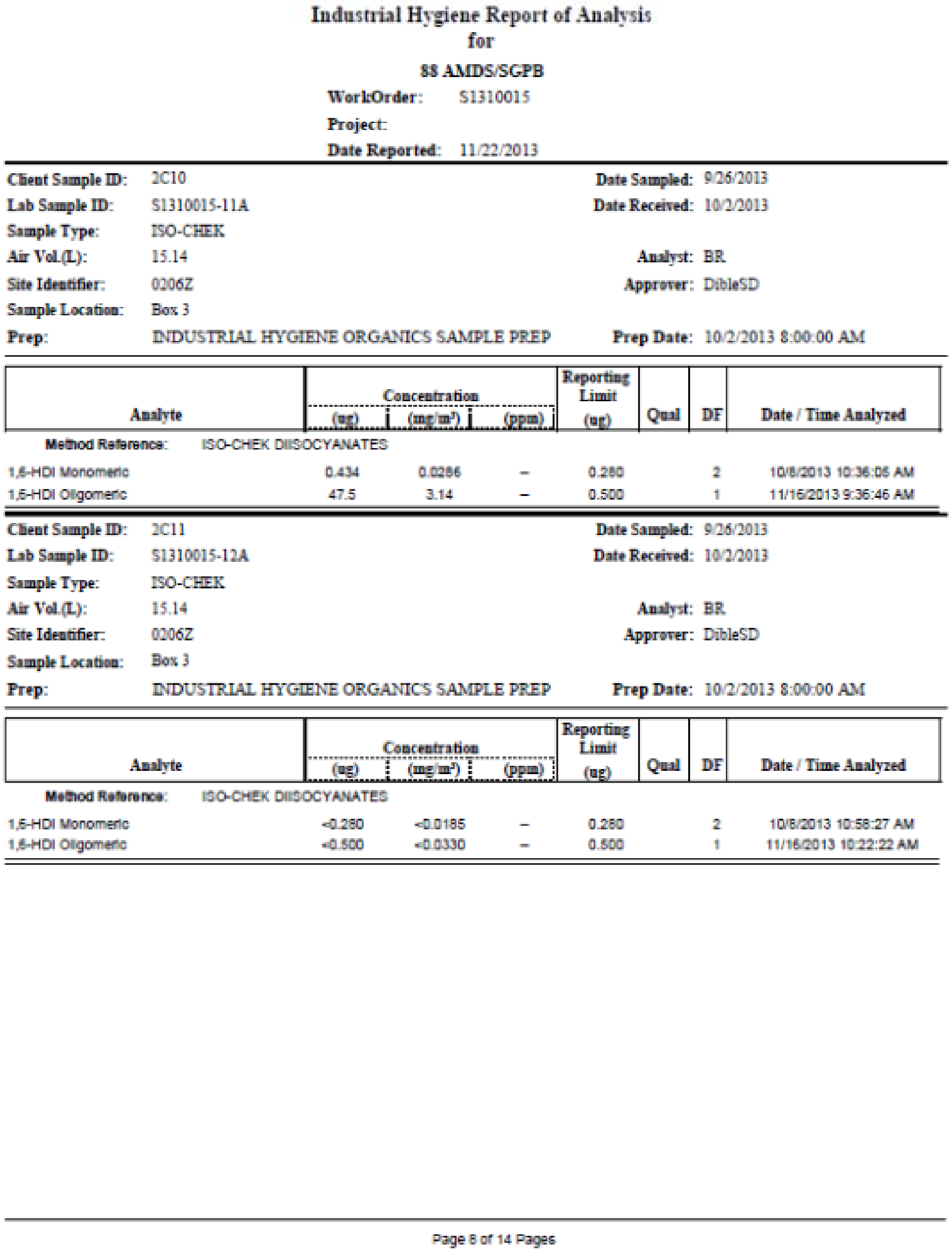

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310015
Project:
Date Reported: 11/22/2013

Client Sample ID: 2C10 **Date Sampled:** 9/26/2013
Lab Sample ID: S1310015-11A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 15.14 **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location: Box 3
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m³)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	0.434	0.0286	–	0.280		2	10/8/2013 10:36:05 AM
1,6-HDI Oligomeric	47.5	3.14	–	0.500		1	11/16/2013 9:36:46 AM

Client Sample ID: 2C11 **Date Sampled:** 9/26/2013
Lab Sample ID: S1310015-12A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 15.14 **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location: Box 3
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m³)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0185	–	0.280		2	10/8/2013 10:58:27 AM
1,6-HDI Oligomeric	<0.500	<0.0330	–	0.500		1	11/16/2013 10:22:22 AM

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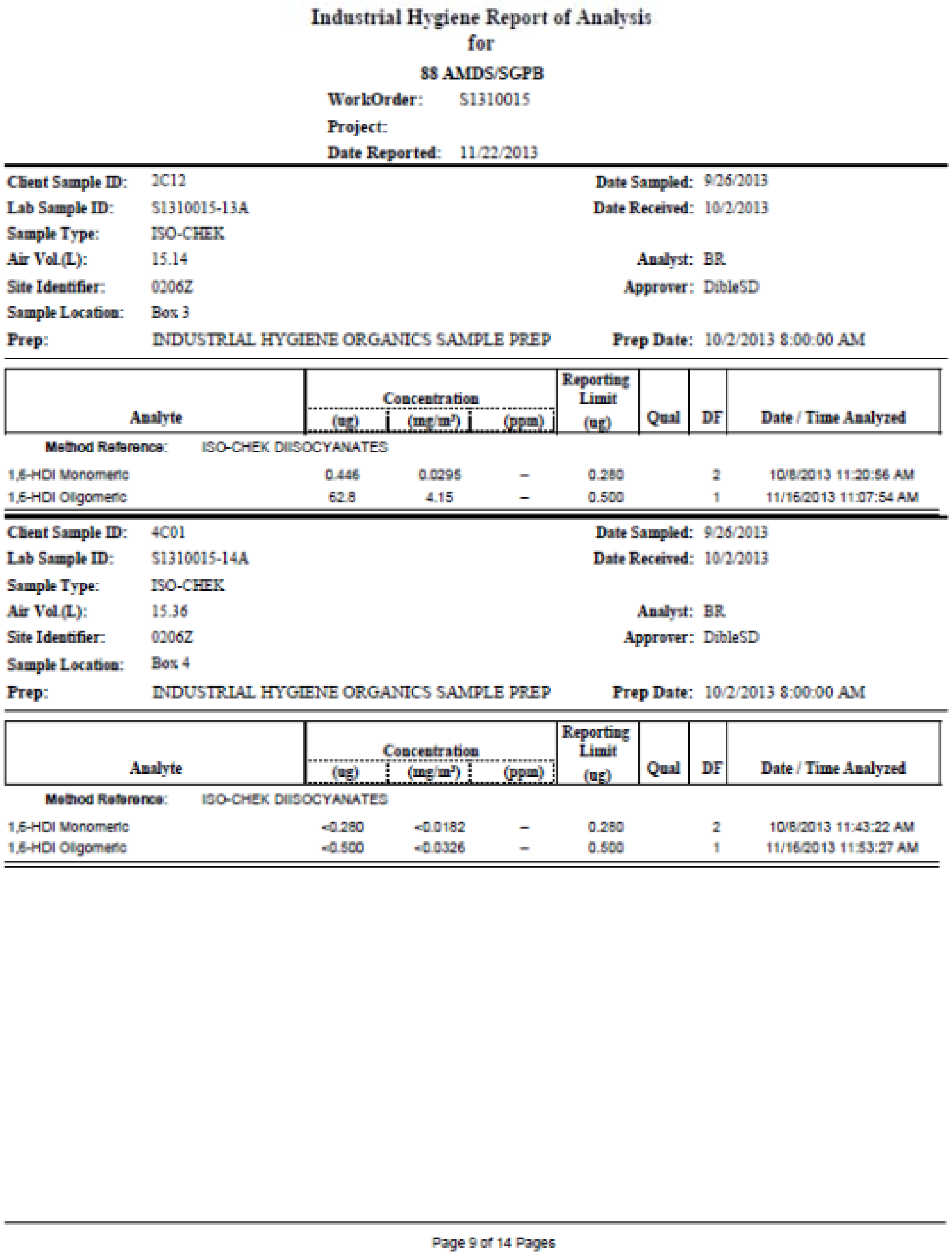

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310015
Project:
Date Reported: 11/22/2013

Client Sample ID: 2C12 **Date Sampled:** 9/26/2013
Lab Sample ID: S1310015-13A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 15.14 **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location: Box 3
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m³)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	0.446	0.0295	–	0.260		2	10/8/2013 11:20:56 AM
1,6-HDI Oligomeric	62.8	4.15	–	0.500		1	11/16/2013 11:07:54 AM

Client Sample ID: 4C01 **Date Sampled:** 9/26/2013
Lab Sample ID: S1310015-14A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 15.36 **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location: Box 4
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m³)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.260	<0.0182	–	0.260		2	10/8/2013 11:43:22 AM
1,6-HDI Oligomeric	<0.500	<0.0326	–	0.500		1	11/16/2013 11:53:27 AM

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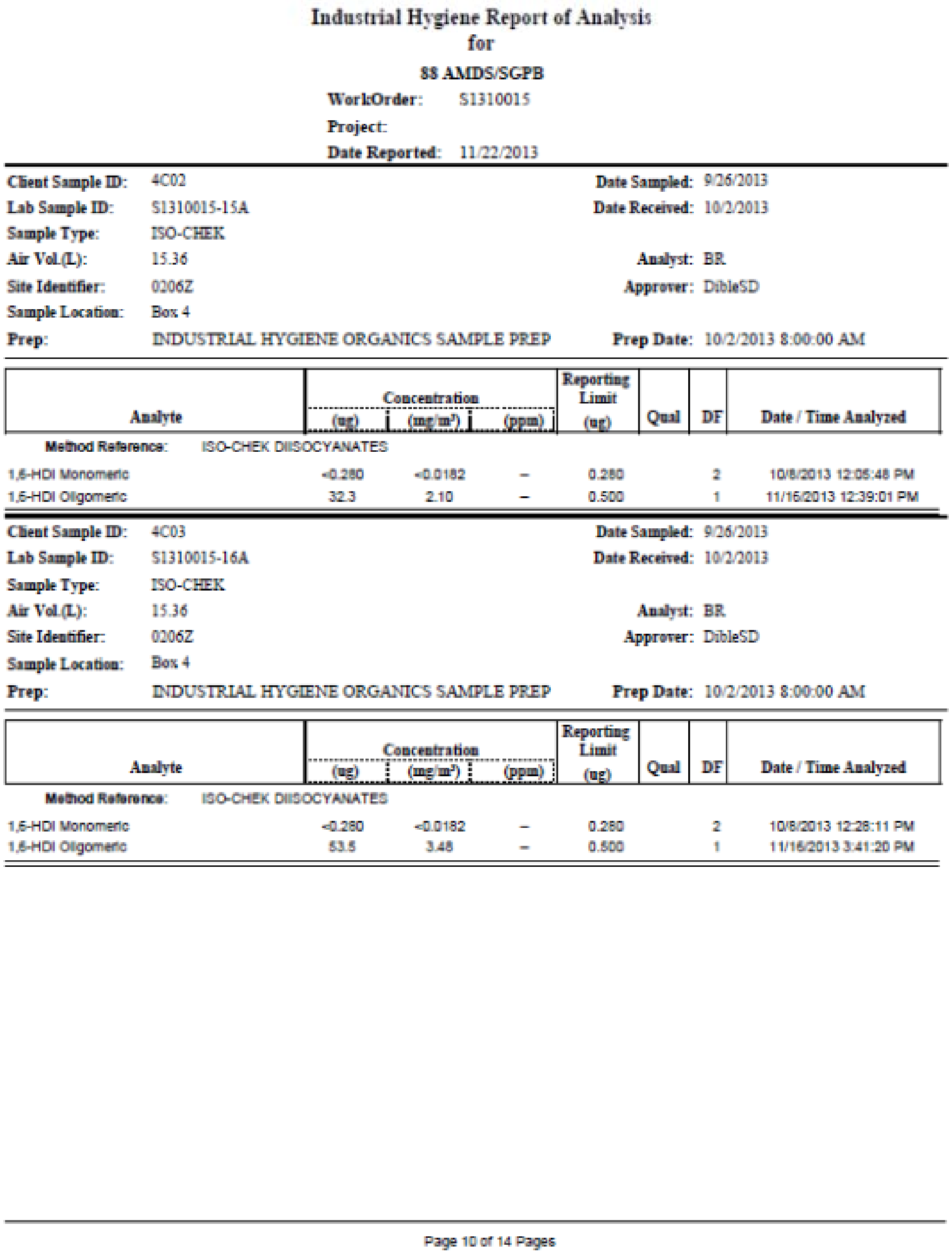

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310015
Project:
Date Reported: 11/22/2013

Client Sample ID:	4C02	**Date Sampled:**	9/26/2013
Lab Sample ID:	S1310015-15A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	15.36	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:	Box 4		
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	(mg/m³)	(ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0182	--	0.280		2	10/8/2013 12:05:48 PM
1,6-HDI Oligomeric	32.3	2.10	--	0.500		1	11/16/2013 12:39:01 PM

Client Sample ID:	4C03	**Date Sampled:**	9/26/2013
Lab Sample ID:	S1310015-16A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	15.36	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:	Box 4		
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	(mg/m³)	(ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0182	--	0.280		2	10/8/2013 12:28:11 PM
1,6-HDI Oligomeric	53.5	3.48	--	0.500		1	11/16/2013 3:41:20 PM

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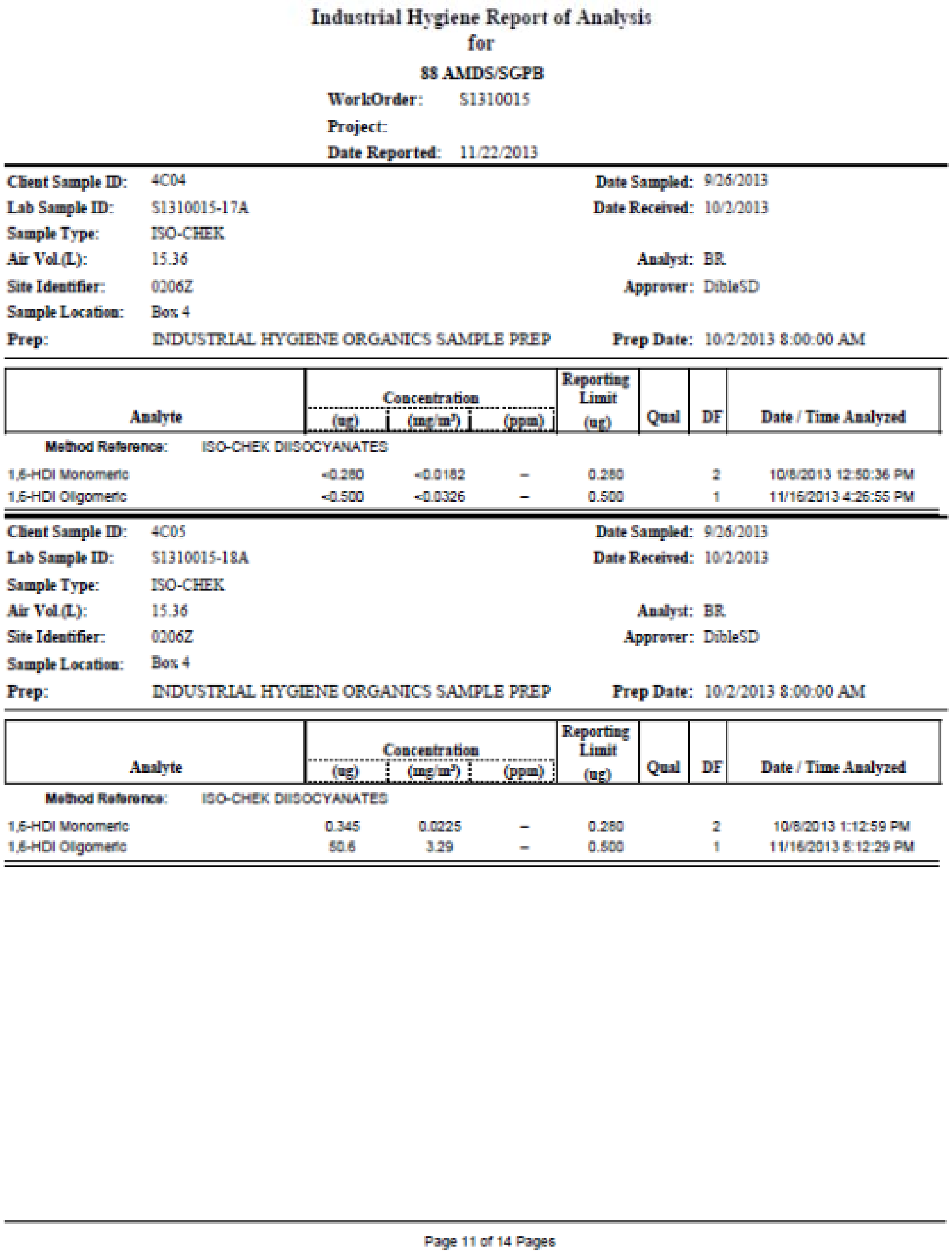

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310015
Project:
Date Reported: 11/22/2013

Client Sample ID: 4C04 **Date Sampled:** 9/26/2013
Lab Sample ID: S1310015-17A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 15.36 **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location: Box 4
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m³)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0182	--	0.280		2	10/8/2013 12:50:36 PM
1,6-HDI Oligomeric	<0.500	<0.0326	--	0.500		1	11/16/2013 4:26:55 PM

Client Sample ID: 4C05 **Date Sampled:** 9/26/2013
Lab Sample ID: S1310015-18A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 15.36 **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location: Box 4
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m³)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	0.345	0.0225	--	0.280		2	10/8/2013 1:12:59 PM
1,6-HDI Oligomeric	50.6	3.29	--	0.500		1	11/16/2013 5:12:29 PM

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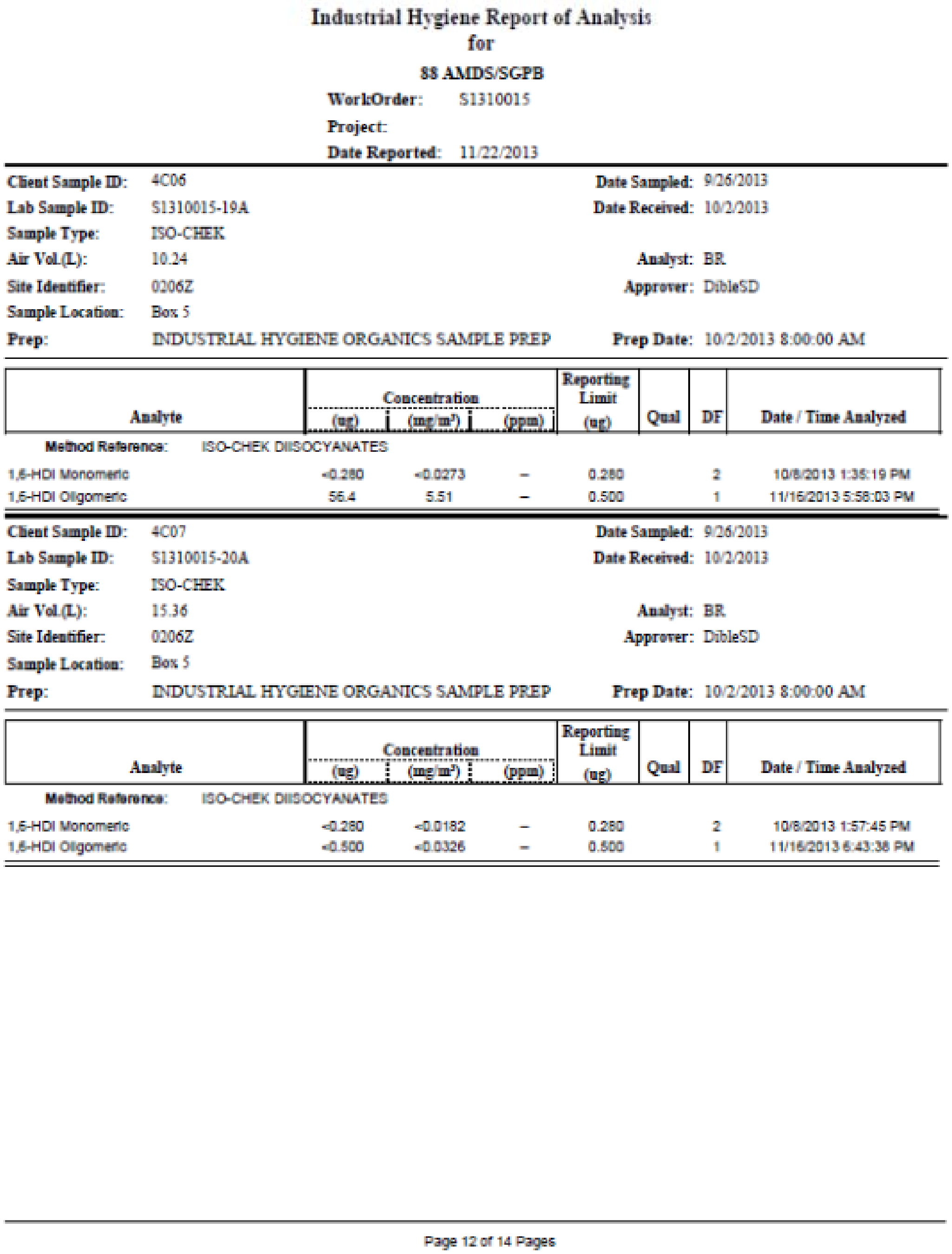

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310015
Project:
Date Reported: 11/22/2013

Client Sample ID: 4C06 **Date Sampled:** 9/26/2013
Lab Sample ID: S1310015-19A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 10.24 **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location: Box 5
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m³)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0273	--	0.280		2	10/8/2013 1:35:19 PM
1,6-HDI Oligomeric	56.4	5.51	--	0.500		1	11/16/2013 5:58:03 PM

Client Sample ID: 4C07 **Date Sampled:** 9/26/2013
Lab Sample ID: S1310015-20A **Date Received:** 10/2/2013
Sample Type: ISO-CHEK
Air Vol.(L): 15.36 **Analyst:** BR
Site Identifier: 0206Z **Approver:** DibleSD
Sample Location: Box 5
Prep: INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP **Prep Date:** 10/2/2013 8:00:00 AM

Analyte	Concentration			Reporting Limit	Qual	DF	Date / Time Analyzed
	(ug)	(mg/m³)	(ppm)	(ug)			
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0182	--	0.280		2	10/8/2013 1:57:45 PM
1,6-HDI Oligomeric	<0.500	<0.0326	--	0.500		1	11/16/2013 6:43:38 PM

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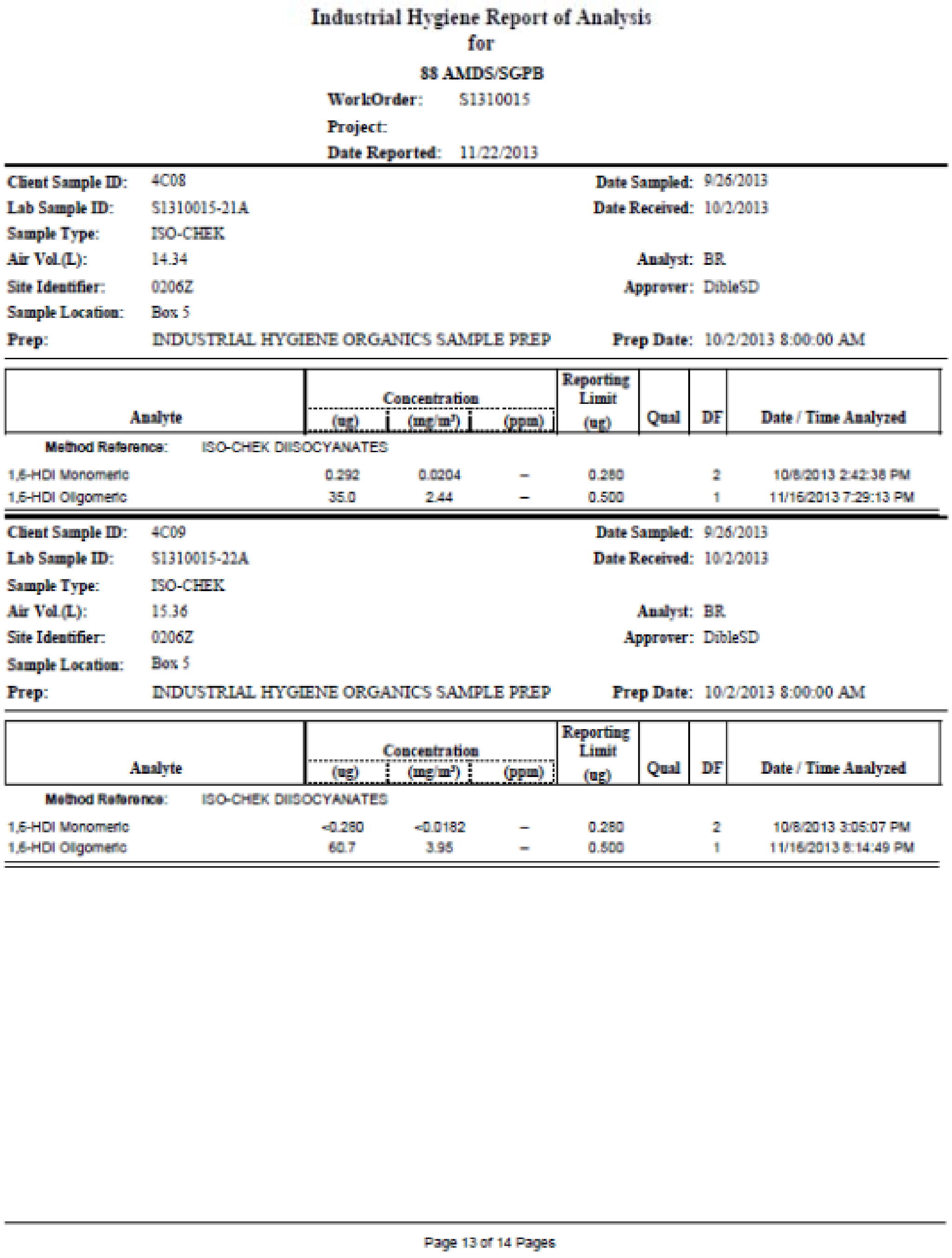

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310015
Project:
Date Reported: 11/22/2013

Client Sample ID:	4C08	**Date Sampled:**	9/26/2013
Lab Sample ID:	S1310015-21A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	14.34	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:	Box 5		
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	**Concentration**			**Reporting Limit (ug)**	**Qual**	**DF**	**Date / Time Analyzed**
	(ug)	**(mg/m³)**	**(ppm)**				
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	0.292	0.0204	--	0.280		2	10/8/2013 2:42:38 PM
1,6-HDI Oligomeric	35.0	2.44	--	0.500		1	11/16/2013 7:29:13 PM

Client Sample ID:	4C09	**Date Sampled:**	9/26/2013
Lab Sample ID:	S1310015-22A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	15.36	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:	Box 5		
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	**Concentration**			**Reporting Limit (ug)**	**Qual**	**DF**	**Date / Time Analyzed**
	(ug)	**(mg/m³)**	**(ppm)**				
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0182	--	0.280		2	10/8/2013 3:05:07 PM
1,6-HDI Oligomeric	60.7	3.95	--	0.500		1	11/16/2013 8:14:49 PM

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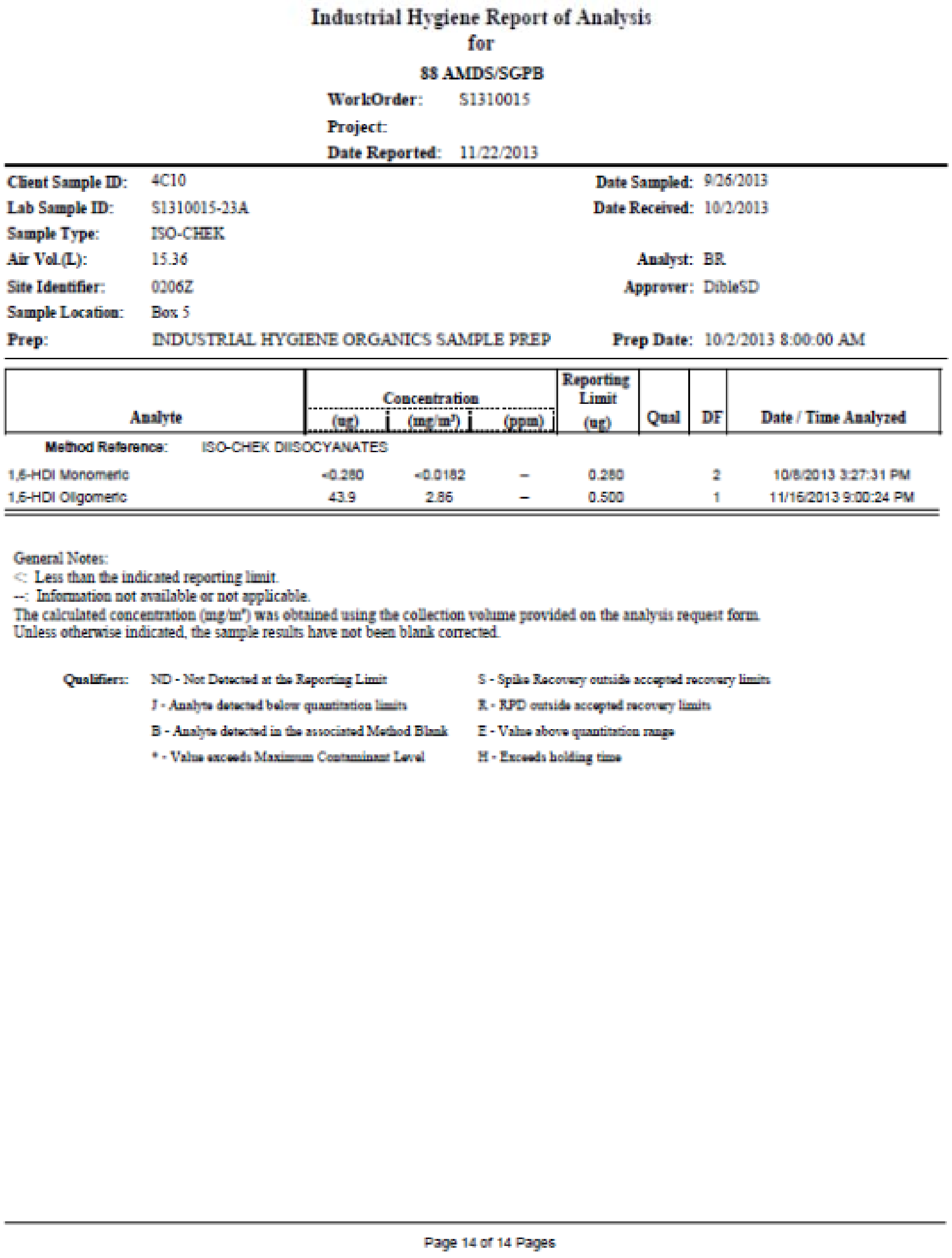

Industrial Hygiene Report of Analysis
for
88 AMDS/SGPB

WorkOrder: S1310015
Project:
Date Reported: 11/22/2013

Client Sample ID:	4C10	**Date Sampled:**	9/26/2013
Lab Sample ID:	S1310015-23A	**Date Received:**	10/2/2013
Sample Type:	ISO-CHEK		
Air Vol.(L):	15.36	**Analyst:**	BR
Site Identifier:	0206Z	**Approver:**	DibleSD
Sample Location:	Box 5		
Prep:	INDUSTRIAL HYGIENE ORGANICS SAMPLE PREP	**Prep Date:**	10/2/2013 8:00:00 AM

Analyte	Concentration (ug)	Concentration (mg/m³)	Concentration (ppm)	Reporting Limit (ug)	Qual	DF	Date / Time Analyzed
Method Reference: ISO-CHEK DIISOCYANATES							
1,6-HDI Monomeric	<0.280	<0.0182	--	0.280		2	10/8/2013 3:27:31 PM
1,6-HDI Oligomeric	43.9	2.86	--	0.500		1	11/16/2013 9:00:24 PM

General Notes:
<: Less than the indicated reporting limit.
--: Information not available or not applicable.
The calculated concentration (mg/m³) was obtained using the collection volume provided on the analysis request form.
Unless otherwise indicated, the sample results have not been blank corrected.

Qualifiers:		
	ND - Not Detected at the Reporting Limit	S - Spike Recovery outside accepted recovery limits
	J - Analyte detected below quantitation limits	R - RPD outside accepted recovery limits
	B - Analyte detected in the associated Method Blank	E - Value above quantitation range
	* - Value exceeds Maximum Contaminant Level	H - Exceeds holding time

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REFERENCES

Abadin, H., and Spoo, W. (1998). *Toxicological Profile for Hexamethylene Diisocyanate.* Agency for Toxic Substance and Disease Registry. Atlanta: U.S. Department of Health and Human Services.

Air Force Corrosion Prevention and Control Office (AFCPCO/RXSSR (2013). Technical Manual- Application and removal of organic coatings, aerospace and non-aerospace equipment, TO 1-1-8.

Andersson, K., Gudehn, A., Levin, J., & Nilsson, C. (1983). A comparative study of solvent and solvent-free sampling methods for airborne 4,4'-diphenylmethane diisocyanate (MDI) generated in polyurethane production. *American Industrial Hygiene Association Journal, 44*(11), 802-808.

ASTM Standard D6561-06, 2011, "Standard Test Method for Determination of Aerosol Monomeric and Oligomeric Hexamethylene Diisocyanate (HDI) in Air with (Methoxy-2-phenyl-1)Piperazine (MOPIP) in the Workplace," ASTM International, West Conshohocken, PA, 2011, DOI: 10.1520/D6561-06R11, www.astm.org.

ASTM Standard D6562-12, 2012, "Standard Test Method for Determination of Gaseous Hexamethylene Diisocyanate (HDI) in Air with 9-(N-methylaminomethyl) Anthracene Method (MAMA) in the Workplace," ASTM International, West Conshohocken, PA, 2012, DOI: 10.1520/D6562-12, www.astm.org.

Bakke, J., Noren, J., Thorud, S., & Aasen, T. (2001). *International consensus report on: Isocyanates- risk assessment and management.* Nordic Council of Ministers.

Batten, T. (2012). *Base level guide for the occupational exposure to isocyanates.* (AFRL-SA-WP-SR-2012-0003).Air Force Research Laboratory, Occupational & Environmental Health Risk Analysis Division.

Bayer Material Science LLC. (2005). The chemistry of polyurethane coatings, A general reference manual. Retrieved 01/19, 2014, from http://bayermaterialsciencenafta.com/resources/d/document.cfm?Mode=view&f=729593C3-97A4-CC14-F31CED5AFF5DF5BA&d=72977823-CCF4-8B0D-003BA154575F4E80&u=yes

Bello, D., Streicher, R. P., Liu, Y. C., Sparer, J., Young, F., & Woskie, S. R. (2002). Field comparison of impingers and treated filters for sampling of total aliphatic isocyanates with the MAP reagent. *AIHA Journal : A Journal for the Science of Occupational and Environmental Health and Safety, 63*(6), 790-796.

Bello, D., Woskie, S. R., Streicher, R. P., Liu, Y., Stowe, M. H., Eisen, E. A., . . . Redlich, C. A. (2004). Polyisocyanates in occupational environments: A critical review of exposure limits and metrics. *American Journal of Industrial Medicine, 46*(5), 480-491. doi:10.1002/ajim.20076

Boutin, M., Lesage, J., Ostiguy, C., & Pauluhn, J. (2005). Validation of a solvent-free sampler for the determination of low molecular weight aliphatic isocyanates under thermal degradation conditions. *Journal of Occupational and Environmental Hygiene, 2*(9), 456-461. doi:10.1080/15459620500240626

Brosseau, L., Fang, C., Snyder, C., & Cohen, B. (1992). Particle size distribution of automobile paint sprays. *Applied Occupational and Environmental Hygiene, 7*(9), 607-612.

Carlton, G., & Flynn, M. (1997). Influence of spray painting parameters on breathing zone particle size distributions. *Applied Occupational & Environmental Hygiene, 12*(11), 744-750.

Carlton, G. N., & England, E. C. (2000). Exposures to 1,6-hexamethylene diisocyanate during polyurethane spray painting in the U.S. Air Force. *Applied Occupational and Environmental Hygiene, 15*(9), 705-712. doi:10.1080/10473220050110121

Ceballos, D., Whittaker, S., Yost, M., Dills, R., Bello, D., Thomasen, J., Nylander-French, L., Reeb-Whitaker, C., Peters, P., Weiland, E., & Suydam, W. (2011). A Laboratory Comparison of Analytical Methods Used for Isocyanates. *Analytical Methods, 3(11),* 2478-2487. doi:10.1039/C1AY05225J

Dahlin, J. (2007). *Aerosols of isocyanates, amines, and anhydrides: Sampling and analysis.* (Doctoral Thesis, Stockholm University).

Dahlin, J., Spanne, M., Karlsson, D., Dalene, M., & Skarping, G. (2008). Size-separated sampling and analysis of isocyanates in workplace aerosols. part I. denuder--cascade impactor sampler. *The Annals of Occupational Hygiene, 52*(5), 361-374. doi:10.1093/annhyg/men017; 10.1093/annhyg/men017

Deft, Inc. (2011). Polyurethane material safety data sheets. Deft Chemical Corporation, Irvine, CA.

Ekman, J., Levin, J., Lindahl, R., Sundgren, M., & Ostin, A. (2002). Comparison of sampling methods for 1,6-hexamethylene diisocyanate (HDI) in a commercial spray box. *Analyst, 127*(1), 169-173.

England, E., Carlton, G., & Greebon, K. (1999). *Assessing worker exposures during polyurethane paint application: Industrial hygiene field guidance for* *bioenvironmental engineers.* (No. IERA-RS-BR-TR-1999-0009).Institute for Environment, Safety, and Occupational Health Risk Analysis.

England, E., Key-Schwartz, R., Lesage, J., Carlton, G., Streicher, R., & Song, R. (2000a). Comparison of sampling methods for monomer and polyisocyanates of 1,6-hexamethylene diisocyanate during spray finishing operations. *Applied Occupational and Environmental Hygiene, 15*(6), 472-478. doi:10.1080/104732200301250

England, E., Key-Schwartz, R., Lesage, J., Carlton, G., Streicher, R., & Song, R. (2000b). Erratum to: Comparison of sampling methods for monomer and polyisocyanates of 1,6-hexamethylene diisocyanate during spray finishing operations. *Applied Occupational and Environmental Hygiene, 16*(1), 1-1. doi:10.1080/104732201456069

Enterprise Environmental, Safety, and Occupational Health – Management Information System (EESOH-MIS)(2012). Computer software. CACI International Inc, Panama City FL.

Fent, K., Jayaraj, K., Gold, A., Ball, L., & Nylander-French, L. (2006). Tape-strip Sampling for Measuring Dermal Exposure to 1-6-Hexamethylene Diisocyanate. *Scandinavian Journal of Work, Environment & Health* , 225-231.

Gylestam, D. (2012). *Isocyanates: Methodology for gas and particle generation, sampling, and detection.* (Doctoral Thesis, Stockholm University).

Gylestam, D., Riddar, J. B., Karlsson, D., Dahlin, J., Dalene, M., & Skarping, G. (2013). Dry sampling of gas-phase isocyanates and isocyanate aerosols from thermal degradation of polyurethane. *The Annals of Occupational Hygiene,* doi:10.1093/annhyg/met046

Huynh, C. K., Vu-Duc, T., & Savolainen, H. (1992). Design and evaluation of a solid sampler for the monitoring of airborne 1,6-hexamethylene diisocyanate (HDI) and its prepolymers in two-component spray painting. *American Industrial Hygiene Association Journal, 53*(3), 157-162.

ISO 17734-1, *Determination of organonitrogen compounds in air using liquid chromatography and mass spectrometry*, (2006E).

ISO 17737, *Workplace atmospheres- guidelines for selecting analytical methods for sampling and analyzing isocyanates in air*, (2012).

Johnson, P. (2013). Isocyanate Exposure Measurement - MDHS 25/3. *Midlands Regional Meeting - Asthma Exposure Isocyanates.* Essington.

Karlsson, D., Dahlin, J., Marand, A., Skarping, G., & Dalene, M. (2005). Determination of airborne isocyanates as di-n-butylamine derivatives using liquid chromatography and tandem mass spectrometry. *Analytica Chimica Acta, 534*, 263-269.

Karlsson, D., Dalene, M., & Skarping, G. (1998). Determination of complex mixtures of airborne isocyanates and amines. Part 5. determination of low molecular weight aliphatic isocyanates as dibutylamine derivatives. *The Analyst, 123*(7), 1507-1512.

Karoly, W. (1998). Stability of diphenylmethane diisocyanate (MDI) on glass fiber filters. *Am. Ind. Hyg. Assoc. J. 59*: 645-647.

Key-Schwartz, R. J. (1995). Analytical problems encountered with NIOSH method 5521 for total isocyanates. *American Industrial Hygiene Association Journal, 56*(5), 474-479. doi:10.1080/15428119591016890

Key-Schwartz, R. J., & Tucker, S. P. (1999). An approach to area sampling and analysis for total isocyanates in workplace air. *American Industrial Hygiene Association Journal, 60*(2), 200-207. doi:10.1080/00028899908984436

Maitre, A., Leplay, A., Perdrix, A., Ohl, G., Boinay, P., Romazini, S., & Aubrun, J. (1996). Comparison between solid sampler and impinger for evaluation of occupational exposure to 1,6-hexamethylene diisocyanate polyisocyanates during spray painting. *American Industrial Hygiene Association Journal, 57*(2), 153-160.

Marand, A., Dahlin, J., Karlsson, D., Skarping, G., & Dalene, M. (2004). Determination of technical grade isocyanates used in the production of polyurethane plastics. *Journal of Environmental Monitoring : JEM, 6*(7), 606-614. doi:10.1039/b402775b

Marand, A., Karlsson, D., Dalene, M., & Skarping, G. (2005). Solvent-free sampling with di-n-butylamine for monitoring of isocyanates in air. *Journal of Environmental Monitoring : JEM, 7*(4), 335-343. doi:10.1039/b414761h

NIOSH. (1994). *NIOSH Method 5521, Isocyanates, Monomeric.* Cincinnati: National Institute for Occupational Safety and Health.

-----. (1995). *Guidelines for Air Sampling and Analytical Method Development and Evaluation.* Cincinnati: US Department of Health and Human Services.

-----. (1996). *NIOSH ALLERT: Preventing Asthma and Death from Diisocyanate Exposure.* Atlanta: Center for Disease Control.

-----. (1998). *NIOSH Method 5522, Isocyanates.* Cincinnati: National Institute for Occupational Safety and Health.

-----. (2003). *NIOSH Method 5525, Isocyanates, Total (MAP).* Cincinnati: National Institute for Occupational Safety and Health.

Omega Specialty Instrument Co. (2006, 9). *ISO-CHEK® Sampling Protocol*. Retrieved 12 2012, from http://www.omegaspec.com/kbase/ShowKbase.asp?Article=203

OSHA. (2013). *National Emphasis Program - Occupational Exposure to Isocyanates.* Washington DC: US Department of Labor.

-----. (1989). *OSHA Method 42, Diisocyanates.* Salt Lake City : Occupational Safety and Health Administration.

Rando, R. J., & Poovey, H. G. (1999). Development and application of a dichotomous vapor/aerosol sampler for HDI-derived total reactive isocyanate group. *American Industrial Hygiene Association Journal, 60*(6), 737-746. doi:10.1080/00028899908984496

Rando, R.J.; Poovey, H.G.; Mokadam, D. (2001). Evaluation of the ISOCHEK Sampler for Measurement of Monomers and Prepolymers of TDI and MDI, Project 155, Reference 11415. International Isocyanate Institute, Inc., Manchester, UK.

Reeb-Whitaker, C., Whittaker, S. G., Ceballos, D. M., Weiland, E. C., Flack, S. L., Fent, K. W., . . . Nylander-French, L. A. (2012). Airborne isocyanate exposures in the collision repair industry and a comparison to occupational exposure limits. *Journal of Occupational and Environmental Hygiene, 9*(5), 329-339. doi:10.1080/15459624.2012.672871; 10.1080/15459624.2012.672871

Roh, Y., Streicher, R., & Ernst, M. (2000). Development of a new approach for total isocyanate determination using the reagent 9-anthracenylmethyl 1-piperazinecarboxylate. *The Analyst, 125*, 1691-1696.

Rudzinski, W. E., Norman, S., Dahlquist, B., Greebon, K. W., Richardson, A., Locke, K., & Thomas, T. (1996). Evaluation of 1-(9-anthracenylmethyl) piperazine for the analysis of isocyanates in spray-painting operations. *American Industrial Hygiene Association Journal, 57*(10), 914-917. doi:10.1080/15428119691014422

Rudzinski, W. E., Yin, J., England, E., Carlton, G., Key-Schwartz, R., & Lesage, J. (2001). A comparison of solid sampler methods for the determination of hexamethylene-based isocyanates in spray-painting operations. *AIHAJ : A Journal for the Science of Occupational and Environmental Health and Safety, 62*(2), 246-250.

Schaeffer, J. W., Sargent, L. M., Sandfort, D. R., & Brazile, W. J. (2013). A comparison of two sampling methods for the detection of airborne methylene bisphenyl diisocyanate. *Journal of Occupational and Environmental Hygiene, 10*(4), 213-221. doi:10.1080/15459624.2013.766546; 10.1080/15459624.2013.766546

Sigma-Aldrich Co. LLC. (2013). *ASSET^{TM} EZ4-NCO Dry Sampler for Isocyanates*. Retrieved Janurary 2014, from Sigma-Aldrich: http://www.sigmaaldrich.com/analytical-chromatography/air-monitoring/asset-nco-sampler.html

Streicher, R. P., Arnold, J. E., Ernst, M. K., & Cooper, C. V. (1996). Development of a novel derivatization reagent for the sampling and analysis of total isocyanate group in air and comparison of its performance with that of several established reagents. *American Industrial Hygiene Association Journal, 57*(10), 905-913. doi:10.1080/15428119691014413

Streicher, R. P., Reh, C. M., Key-Schwartz, R. J., Schlecht, P. C., Cassinelli, M. E., & O'Connor, P. F. (2000). Determination of airborne isocyanate exposure: Considerations in method selection. *AIHAJ : A Journal for the Science of Occupational and Environmental Health and Safety, 61*(4), 544-556.

Supelco Analytical. (2013). *Extraction and Analysis of ASSET^{TM} EZA-NCO Dry Sampler Rev 1.5.* Bellefonte: Supelco.

Thomasen, J. M., Fent, K. W., Reeb-Whitaker, C., Whittaker, S. G., & Nylander-French, L. A. (2011). Field comparison of air sampling methods for monomeric and polymeric 1,6-hexamethylene diisocyanate. *Journal of Occupational and Environmental Hygiene, 8*(3), 161-178. doi:10.1080/15459624.2011.555711; 10.1080/15459624.2011.555711

Tinnerberg, H., Karlsson, D., Dalene, M., & Skarping, G. (1997). Determination of toluene diisocyanate in air using di-n-butylamine and 9-N-methyl-aminomethyl-anthracene as derivatization reagents. *Journal of Liquid Chromatography & Related Technologies, 20*(14), 2207-2219.

WADOSH. (2013). *Isocyanates NEP.* Olympia: Washington Division of Occupational Safety and Health.

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14. ABSTRACT

During this study, a field evaluation of a new sampling method using di-n-butylamine for the determination of airborne monomeric and oligomeric 1,6-hexamethylene diisocyanate (HDI) was performed. The Supelco ASSET EZ4-NCO Dry Sampler was compared to the Omega Specialty Instrument Co. ISO-CHEK sampler. Three specific questions were addressed: 1) can HDI oligomers be quantified using HPLC-MS; 2) do ASSET and ISO-CHEK samplers collect equivalent HDI monomer & oligomer concentrations; and 3) what is the relative cost of ASSET samplers verse ISO-CHEK. Side-by-side HDI air sampling was conducted during polyurethane spray painting operations. ASSET samplers were analyzed by HPLC-MS for HDI monomer and oligomers, including biuret and isocyanurate. The ASSET sampler collected significantly higher levels of HDI monomers, indicating ISO-CHEK samplers potentially underestimate true monomer exposures. HDI oligomer results were inconclusive. Finally, the analytical cost for the ASSET sampler was determined to be 50 percent less than ISO-CHEK resulting in a cost savings of $32 K over 5 years.

15. SUBJECT TERMS
Polyurethane, isocyanates, 1,6-hexamethylene diisocyanate, HDI, ASSET EZ4 NCO, ISO-CHEK, ISO-CHECK, di-n-butylamine, oligomers

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