

NIOSH OSHA

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- Abstract -

Assessment of total isocyanates by OSHA and NIOSH analytical methods: accuracy and precision and airborne concentrations by process

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The purpose of this study was to compare performances of two analytical methods, the OSHA 42 and the NIOSH 5522, of quantifying total isocyanates in air. These methods were compared in terms of accuracy and precision and the detection limits using four(4) spiked samples in each of four(4) concentration levels which ranged from 0.25 to 2.0 times of the ACGIH TLV-TWA.

In addition, two methods were used to assess airborne concentrations of total isocyanates at the following processes including autobody spray painting, furniture spray painting, polyurethane foaming, urethane adhesion, UV coating, and pigment mixing.

The results of this study showed that the NIOSH 5522 method was better than the OSHA 42

method in terms of accuracy, precision, and detection limit for quantifying airborne total isocyanates. It was also clear that the NIOSH method was capable of detecting not only monomeric but also non-monomeric isocyanates. The results of air concentrations of total isocyanates among processes studied indicate that some processes may exceed the recommended level of isocyanates.

In addition, to evaluate toxicological effects of total isocyanates, it is recommended to consider additive effects of isocyanates present in mixtures.

Key Words : 2,4-TDI, 2,6-TDI, HDI, MDI, NIOSH 5522 method, OSHA 42 method,

† : 505 가

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I. 머 리 말

이소시아네이트는 단단한 재질의 단열재, 유연성 있는 재질의 쿠션, 내구성있는 코팅제, 그리고 접착제 등을 포함한 폴리우레탄 제조와 카바메이트계 농약 제조 등에 상업적으로 광범위하게 사용하는 화학물질로서 중요한 작용기(-NCO)이다. 톨루엔 디이소시아네이트(toluene diisocyanate, 이하 TDI), 헥사메틸렌 디이소시아네이트(hexamethylene diisocyanate, 이하 HDI), 메틸렌 비스페닐 디이소시아네이트(methylene bisphenyl diisocyanate, 이하 MDI) 등이 대표적인 이소시아네이트 물질로 알려져 있다. 이중 TDI가 가장 많이 사용되는데 2,4-TDI와 이성체인 2,6-TDI가 80 : 20 또는 65 : 35의 비율로 함유된 혼합물이 상업적으로 많이 사용되고 있다(Gilbert, 1988). 이들 화합물이 근로자에 노출되면 여러 호흡기 질환을 발생시킬 수 있다(Musk et al., 1988). 특히 TDI에 노출되면 점막을 자극해 폐기능을 점차적으로 손상시키고(Wegman et al., 1982) 감작성을 띠며 알러지성 천식의 원인이 된다(Hagmar et al., 1987). 더욱이 상품화된 TDI는 동물실험에서 발암성이 입증되었다(NTP, 1986).

2,4-TDI, HDI, MDI에 대한 노출기준은 미국 산업위생전문가협회(American Conference of Governmental Industrial Hygienists, 이하 ACGIH)에서는 시간가중 평균 허용농도로 각각 0.036 mg/m³, 0.034 mg/m³, 0.051 mg/m³로 권고했고, 2,6-TDI의 경우 2,4-TDI와 동일한 기준으로 제정할 계획이다(ACGIH, 1998). 노동부에서는 2,6-TDI와 HDI의 경우 노출기준이 규정되어 있지 않고 있으며 2,4-TDI와 MDI는 ACGIH 노출기준과 동일하게 각각 시간가중 평균 허용농도를 0.04 mg/m³, 0.055 mg/m³로 규정하고 있다(노동부, 1998a).

이들은 모두 단량체(monomer)형태의 이소시아네이트에 대한 규제를 의미하고 있으나, 최근 공기 중 이소시아네이트류의 연구경향은 비단량체(non-monomeric) 이소시아네이트류의 노출평가에 초점을 두고 있다

(Silk et al., 1983; Janko et al., 1992; Vandenplas et al., 1992). 비단량체 이소시아네이트류란 단량체와 동시에 합성되는 oligomeric species, 폴리우레탄 제조 시 원료 물질인 휘발성 단량체 대신 사용하는 prepolymers, 반응 중에 생기는 부 반응 생성물들 또는 열분해 생성물들을 말하는데 이런류의 물질들은 분무, 절단 또는 열에 의해 공기 중으로 방출될 수 있다(Streicher et al., 1996). 또한 연구결과 비단량체 이소시아네이트류에 대한 건강장해는 단량체의 노출과 동일하게 나타나는 것으로 확인되었다(Lesage et al., 1992; Vandenplas et al., 1993). 따라서 단지 단량체 뿐만 아니라 비단량체의 이소시아네이트류를 포함한 총 이소시아네이트 반응기에 대한 정확한 평가 방법이 절실히 요구되어, 국외에서는 이미 연구가 활발히 진행되고 있으나(Rando et al., 1995; Rudzinski et al., 1996; Wu et al., 1997), 현재 국내에서는 비단량체를 포함한 총 이소시아네이트에 대한 연구는 찾아보기 어렵다.

이소시아네이트류의 측정과 분석방법은 일반적으로 다양한 이차 아민의 유도체화 시약과 반응시켜 우레아 유도체 물질을 만든 후 액체크로마토그래피(High Performance Liquid Chromatography, 이하 HPLC)로 분석하는 것을 기본으로 한다(Sangö와 Zimerson, 1980). 지금까지 보고된 공기 중 이소시아네이트 평가 방법으로는 Marcali 방법(Marcali, 1957), Method 25 for the Determination of Hazardous Substances(MDHS 25)(Health and Safety Executive, 1987), OSHA 42 방법(OSHA, 1989), NIOSH 5521 방법(NIOSH, 1994), NIOSH 5522 방법(NIOSH, 1996) 등 있다.

현재 국내 작업환경측정기관에서 가장 많이 사용하는 공기 중 이소시아네이트류의 분석방법은 Marcali(1957)에 의해 개발된 비색법과 OSHA 42 방법 그리고 NIOSH 5521 방법이다. 이중 Marcali 비색법은 임핀저를 이용해 이소시아네이트를 포집한 후 발색시켜 분광광도계로 그 흡수도를 측정하는 방법이다. 그러나 1998년 산업안전보건법 제 95조 규칙 별표 12의

가

HPLC

Marcali (, 1994)

(, 1998b), OSHA NIOSH

가 (, 1997)가 .

HPLC ,

가 가 가 OSHA 42 NIOSH 5521

(Purnell Walker, 1985). OSHA 42 1-2

(1- 2Pyridylpiperazine, 1- 2PP) .

HPLC .

aerosol prepolymers OSHA 42 NIOSH 5522

가 , 가 ,

가 가

(Czarnecki, 1992). mist aerosol type

가 .

가

(OSHA, 1989). NIOSH 5521

(methoxyphenylpiperazine, MPP)

1.

HPLC

가 airborne ,

(Czarnecki, 1992; 15 ℓ 0.25, 0.5, 1.0, 2.0

Miles Corporate Industrial Hygiene Laboratory, 4 OSHA 42 NIOSH

1992), OSHA 42 가 5522

(, 1997), 32 .

NIOSH 5521 oligomeric

25

(Key Schwartz, 1995), NIOSH 가 11 , , ,

가 , , ,

(dimethyl sulfoxide, DMSO) 1998 9 1998 10

(tryptamine, TRYP)

HPLC 164 .

5522 (NIOSH, 1996).

2.

1)

(1) OSHA 42

1- 2PP 0.2 mg/ml

0.5 ml

three piece cassette holder

open face

1 l/min, 240~360

(MSA, Model Escort Elf, U.S.A.)

(SKC,

Model 712, U.S.A.)

HPLC(Waters M510, U.S.A.)

Table 1

Table 1. Operating conditions of HPLC used for analysis of isocyanates

| Variance | Conditions |
|------------------|---|
| Instrument | HPLC Waters M510 |
| Column | Nova-pak C18 (3.9 mm×150 mm×4 μm) [†] Symmetry C18 (3.9 mm×150 mm×5 μm) [‡] |
| Mobile phase | Acetonitrile : 0.01 M Ammonium acetate (pH 6.2) = 30 : 70 [†] Acetonitrile : 0.07 M Sodium acetate trihydrate (pH 5.5) = 40 : 60 [‡] |
| Flow rate | 1.0 ml/min |
| Injection volume | 10 μl |
| Detector | UVD, 254 nm |

Note : UVD=ultra violet detector; †=OSHA 42 method; ‡=NIOSH 5522 method;
HPLC=high performance liquid chromatography

가

(Aldrich chemical Co., Milwaukee, Wis., U.S.A.) 50 μl 가 TRYP

HPLC(Waters M510, U.S.A.)

1

2)

(1) OSHA 42

SUPELCO

(Bellefonte, Pa.)

2,4- TDI, 2,6- TDI, HDI, MDI

N,N' - (2- Methyl- 1,3- phenylene)bis[4- (2- pyridinyl)- 1- piperazinecarboxamide],N,N' - (4- Methyl- 1, 3- phenylene)bis[4- (2- pyridinyl)- 1- piperazinecarboxamide], N,N' - 1,6- Hexanedylbis[4- (2- pyridinyl) piperazinecarboxamide], N,N' - (Methylenediphenylene)bis[4- (2- pyridinyl)- 1- piperazinecarboxamide]

1:1:1:1 (Aceto-nitrile, ACN, Tedia CO., Fairfield, O., U.S.A.)

0.027~0.694 μg

(2) NIOSH 5522

가.

0.0025 mole 99 % TRYP(Sigma chemical CO. Louis, Mo., U.S.A.) 300 ml

(Tedia CO., Fairfield, O., U.S.A.) TRYP

60℃ 가

0.001 mole 가

(Junsei chemical Co., Tokyo, Japan) n- (Tedia CO., Fairfield, O., U.S.A.)

(Electro- thermal, IA 9100, U.S.A.)

Table 2

Table 2. Melting points of tryptamine derivatives

| Isocyanate | Tryptamine derivative | Melting point(℃) |
|------------|--|------------------|
| 2,4- TDI | toluene- 2,4- diisocyanate- tryptamine | 216~219 |
| 2,6- TDI | toluene- 2,6- diisocyanate- tryptamine | 298~301 |
| HDI | hexamethylene diisocyanate- tryptamine | ~270 |
| MDI | 4,4'- methylene diphenylisocyanate- tryptamine | 201~201.5 |

Note : TDI=toluene diisocyanate; MDI=methylene bisphenyl diisocyanate;
HDI=hexamethylene diisocyanate

2,4- TDI, 2,6- TDI, HDI, MDI TRYP
1:1:1:1 DMSO
ACN 0.005~0.167 μg

3)
(1) OSHA 42
(Aldrich chemical Co.,
Milwaukee, Wis., U.S.A.) 1- 2PP

(2) NIOSH 5522
OSHA 42
TRYP 0.45 mg/ml DMSO 10 ml 가

4)
% recovery
1 (Taylor,
1987; NIOSH, 1995).

$$= \frac{\text{가}}{\text{가}} \times 100 \dots \dots \dots (1)$$

(coefficient of variation,
CV)
(overall CV, pooled CV)
CV pooled CV 2 3
(Taylor, 1987; NIOSH, 1995).

$$CV = \dots \dots \dots (2)$$

$$Pooled\ CV = \frac{(N_1-1)Sr_1^2 + (N_2-1)Sr_2^2 + \dots + (N_n-1)Sr_n^2}{(N_1-1) + (N_2-1) + \dots + (N_n-1)} \dots (3)$$

N=
Sri=i

SAS package
OSHA 42 NIOSH 5522 가

t- test(α=0.05)

(
ANOVA Duncan

III.

1. 가

, Fig. 1
. 2,4- TDI, 2,6- TDI, HDI, MDI
NIOSH 5522
10.2 , 7.02 , 6.33 , 28.7 OSHA 42
9.08 , 6.04 , 7.46 , 54.2 .

Fig. 2, 3

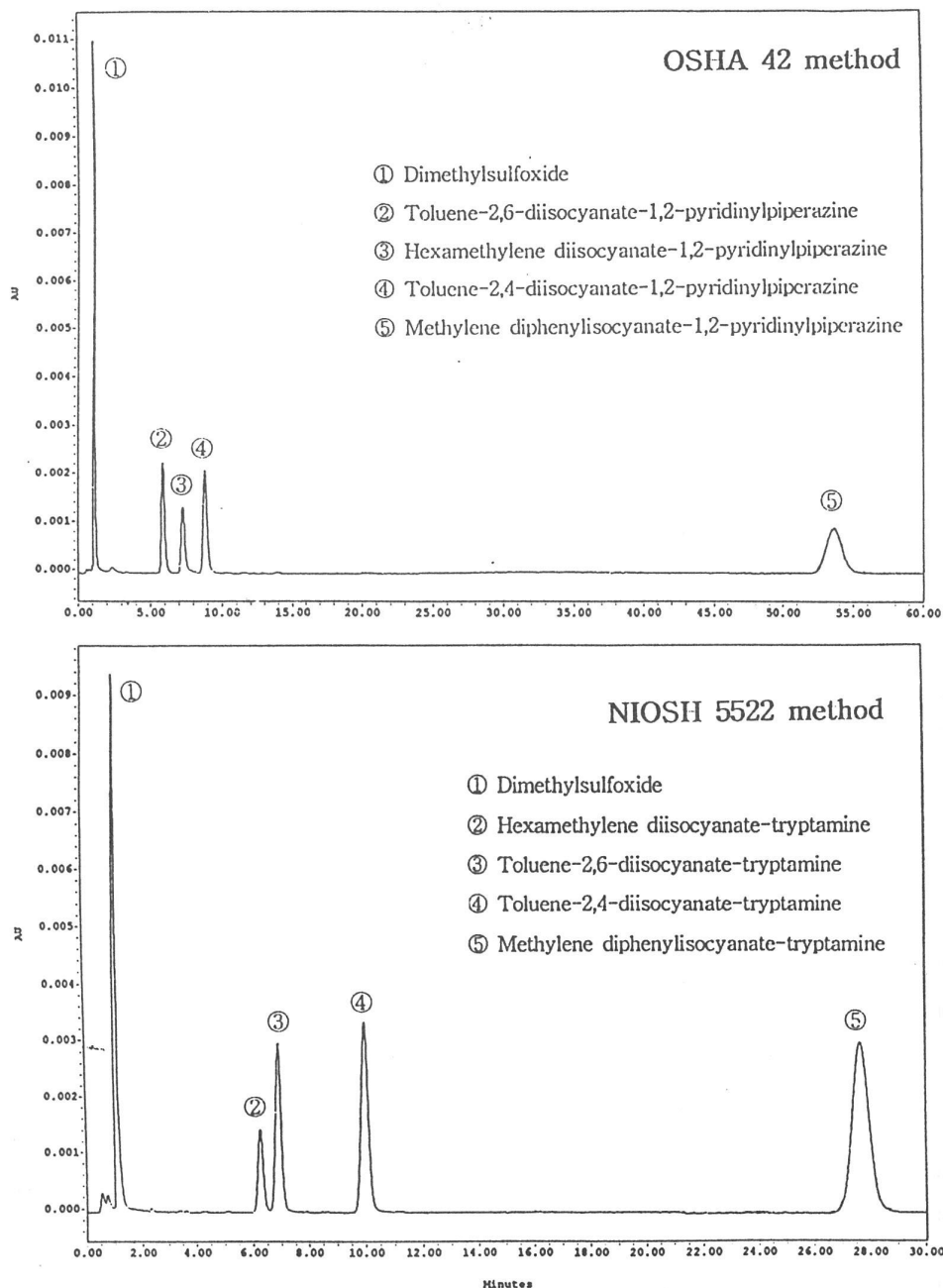
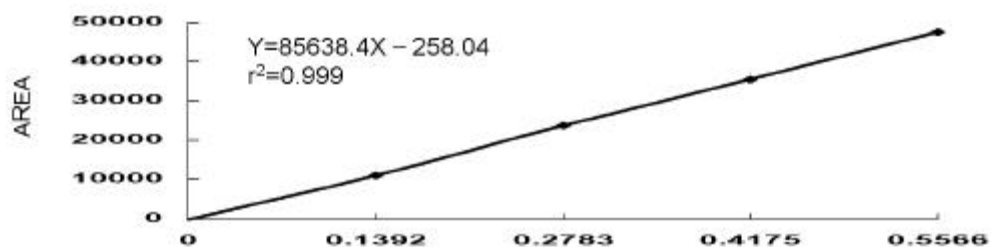
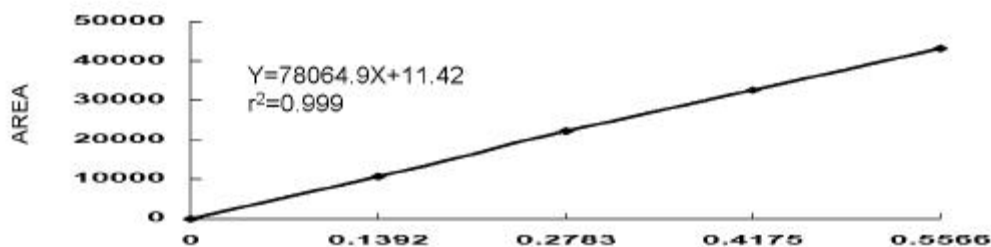


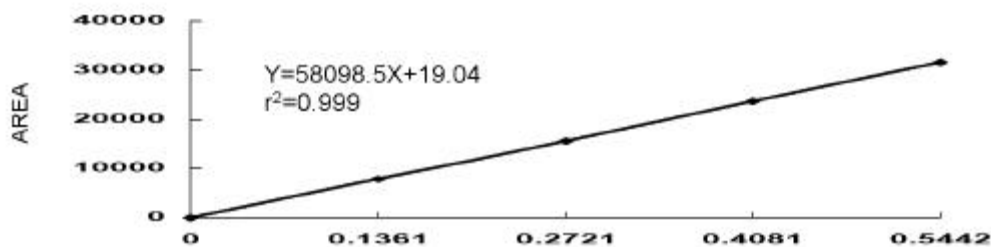
Fig. 1 Chromatograms of isocyanate urea



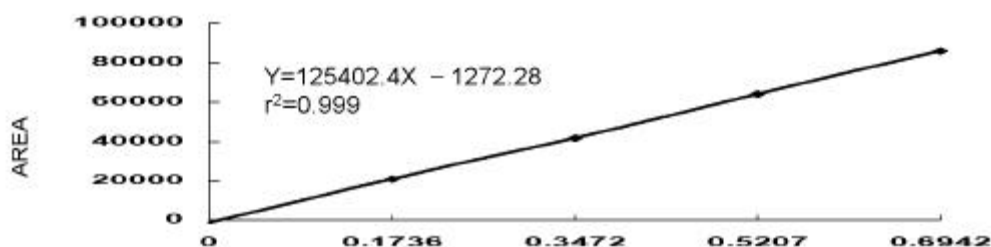
Concentration of 2,4-TDI (ug)



Concentration of 2,6-TDI (ug)



Concentration of HDI (ug)



Concentration of MDI (ug)

Fig. 2. Calibration curves of isocyanate by OSHA 42 method TDI ; toluene diisocyanate, HDI ; hexamethylene diisocyanate, MDI ; methylene bisphenyl diisocyanate

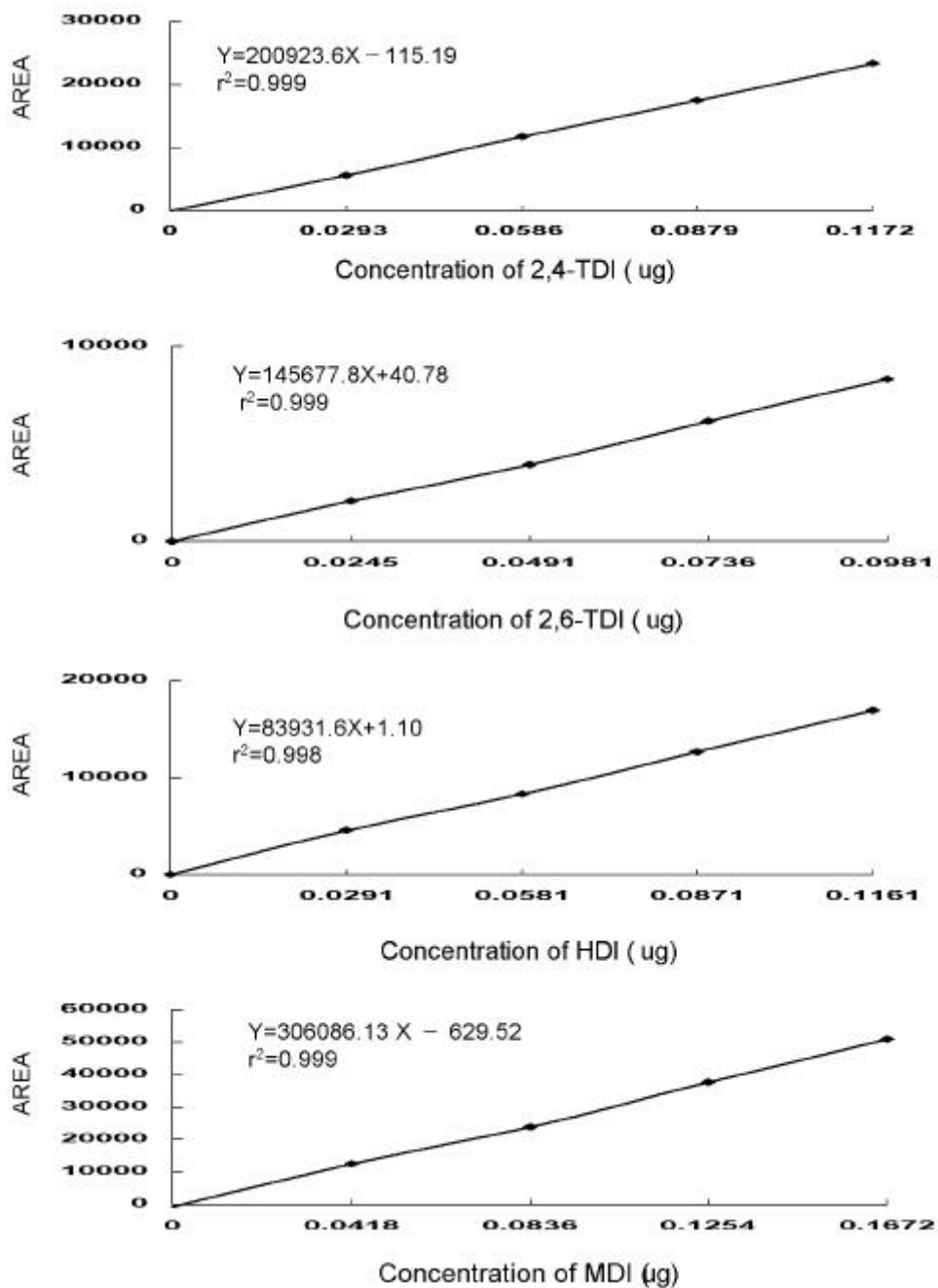


Fig. 3. Calibration curves of isocyanate by NIOSH 5522 method TDI ; toluene diisocyanate, HDI ; hexamethylene diisocyanate, MDI ; methylene bisphenyl diisocyanate

Table 3, 4

Table 3. Accuracy and precision of isocyanates by analytical method

| Isocyanates | Spiked conc.(μg) | N | OSHA 42 method | | | NIOSH 5522 method | | |
|-------------|-------------------------------|----|---|-----------------------------------|-------------------|---|-----------------------------------|-------------------|
| | | | Detected conc. (μg , Mean \pm SD) | Recovery rate (% , Mean \pm SD) | CV (%) | Detected conc. (μg , Mean \pm SD) | Recovery rate (% , Mean \pm SD) | CV (%) |
| 2,4- TDI | 0.135 | 4 | 0.133 \pm 0.002 | 98.50 \pm 1.37 | 1.39 | 0.159 \pm 0.008 | 117.50 \pm 6.23* | 5.30 |
| | 0.271 | 4 | 0.301 \pm 0.015 | 111.15 \pm 5.56* | 5.00 | 0.271 \pm 0.007 | 100.00 \pm 2.52 | 2.52 |
| | 0.541 | 4 | 0.615 \pm 0.015 | 113.60 \pm 2.76* | 2.42 | 0.504 \pm 0.003 | 93.08 \pm 0.56 | 0.60 |
| | 1.0820 | 4 | 1.057 \pm 0.031 | 97.65 \pm 2.88* | 2.95 | 0.907 \pm 0.008 | 83.68 \pm 0.57 | 0.68 |
| | Total | 16 | | 105.23 \pm 8.07 | 3.22 [†] | | 98.56 \pm 13.13 | 2.97 [†] |
| 2,6- TDI | 0.135 | 4 | 0.129 \pm 0.003 | 95.40 \pm 2.19 | 2.30 | 0.142 \pm 0.005 | 104.58 \pm 3.32* | 3.17 |
| | 0.271 | 4 | 0.266 \pm 0.007 | 98.43 \pm 2.69 | 2.73 | 0.272 \pm 0.004 | 101.03 \pm 1.52 | 1.50 |
| | 0.541 | 4 | 0.515 \pm 0.008 | 95.13 \pm 1.52 | 1.60 | 0.525 \pm 0.004 | 97.00 \pm 0.73 | 0.75 |
| | 1.082 | 4 | 0.924 \pm 0.027 | 85.33 \pm 2.52 | 2.95 | 0.976 \pm 0.013 | 90.23 \pm 1.19* | 1.32 |
| | Total | 16 | | 93.57 \pm 5.49 | 2.45 [†] | | 98.21 \pm 5.78* | 1.91 [†] |

Note : TDI=toluene diisocyanate; N=number of samples; conc.=concentration; CV=coefficient of variation; [†]=pooled CV * ; p<0.05 t- test

Table 4. Accuracy and precision of isocyanates by analytical method

| Isocyanates | Spiked conc.(μg) | N | OSHA 42 method | | | NIOSH 5522 method | | |
|-------------|-------------------------------|----|---|-----------------------------------|-------------------|---|-----------------------------------|-------------------|
| | | | Detected conc. (μg , Mean \pm SD) | Recovery rate (% , Mean \pm SD) | CV (%) | Detected conc. (μg , Mean \pm SD) | Recovery rate (% , Mean \pm SD) | CV (%) |
| 2,4- TDI | 0.128 | 4 | 0.125 \pm 0.002 | 98.50 \pm 1.71* | 1.74 | 0.104 \pm 0.003 | 81.83 \pm 2.28 | 2.79 |
| | 0.255 | 4 | 0.258 \pm 0.011 | 101.90 \pm 4.60* | 4.51 | 0.208 \pm 0.006 | 81.58 \pm 2.48 | 3.04 |
| | 0.510 | 4 | 0.509 \pm 0.004 | 99.75 \pm 0.81* | 0.81 | 0.414 \pm 0.010 | 81.20 \pm 1.93 | 2.38 |
| | 1.020 | 4 | 0.943 \pm 0.013 | 92.455 \pm 1.34* | 1.45 | 0.789 \pm 0.021 | 77.30 \pm 2.05 | 2.65 |
| | Total | 16 | | 98.08 \pm 4.29* | 2.56 [†] | | 80.48 \pm 2.74 | 2.73 [†] |
| 2,6- TDI | 0.192 | 4 | 0.175 \pm 0.014 | 91.35 \pm 7.46 | 8.17 | 0.193 \pm 0.005 | 100.73 \pm 2.74 | 2.72 |
| | 0.384 | 4 | 0.362 \pm 0.003 | 94.28 \pm 0.83 | 0.87 | 0.369 \pm 0.010 | 96.05 \pm 2.56 | 2.66 |
| | 0.767 | 4 | 0.724 \pm 0.019 | 94.33 \pm 2.55 | 2.70 | 0.734 \pm 0.005 | 95.65 \pm 0.64 | 0.66 |
| | 1.534 | 4 | 1.427 \pm 0.021 | 92.98 \pm 1.40* | 1.50 | 1.376 \pm 0.025 | 89.63 \pm 1.66 | 1.85 |
| | Total | 16 | | 93.23 \pm 3.81 | 4.39 [†] | | 95.51 \pm 4.47 | 2.14 |

Note : TDI=toluene diisocyanate; N=number of samples; conc.=concentration; CV=coefficient of variation; [†]=pooled CV * ; p<0.05 t- test

1) 가

OSHA 42

2,4- TDI, 2,6- TDI, HDI, MDI 90%

, NIOSH 5522

2,4- TDI, 2,6- TDI, MDI 90%

HDI 80.48%

t- test 2,6- TDI NIOSH 5522

, HDI OSHA 42

(P<0.05).

t- test 2,4- TDI ACGIH 가

0.25 OSHA 42

NIOSH 5522

NIOSH 5522 OSHA

42 (P<0.05).

2,6- TDI 0.25 2.0 OSHA

42 NIOSH 5522

, HDI NIOSH 5522

OSHA 42 (P

<0.05). MDI

가 (P>0.05).

2) 가

OSHA 42

NIOSH 5522 pooled CV가 5%

가 HDI NIOSH 5522

가

3) 가

(LOD) Table 5

2,4- TDI, 2,6- TDI, HDI, MDI 8 , 3 , 1.6

, 1.5 NIOSH 5522 OSHA 42

NIOSH 5522 LOD 2,4- TDI,

2,6- TDI, HDI, MDI 0.1, 0.2, 0.2, 0.3 $\mu\text{g}/\text{sample}$

, OSHA 42, 47

LOD 0.0192, 0.0244, 0.0333, 0.0116 μg

/sample

Table 5. LOD of isocyanates by analytical method

| Method | LOD ($\mu\text{g}/\text{sample}$) | | | |
|-------------------|-------------------------------------|----------|---------|---------|
| | 2,4- TDI | 2,6- TDI | HDI | MDI |
| OSHA 42 method | 0.01753 | 0.01426 | 0.00989 | 0.01343 |
| NIOSH 5522 method | 0.00245 | 0.00568 | 0.00605 | 0.00861 |

Note : TDI=toluene diisocyanate;
HDI=hexamethylene diisocyanate;
MDI=methylene bisphenyl diisocyanate;
LOD : limit of detection 3SE/B
(SE; standard error, B; slope, NIOSH, 1995)

2.

25

가 11

, ,

OSHA 42 NIOSH 5522

2,4- TDI, 2,6- TDI, HDI, MDI

Table 6

OSHA 42 NIOSH 5522

Duncan

Table 6

OSHA 42 2,4- TDI

0.16 $\mu\text{g}/\text{m}^3$, 가

0.43 $\mu\text{g}/\text{m}^3$, 0.73 $\mu\text{g}/\text{m}^3$,

0.13 $\mu\text{g}/\text{m}^3$, 0.36 $\mu\text{g}/\text{m}^3$,

0.21 $\mu\text{g}/\text{m}^3$

. 2,6- TDI

0.23 $\mu\text{g}/\text{m}^3$, 가 1.70 $\mu\text{g}/\text{m}^3$,

1.48 $\mu\text{g}/\text{m}^3$, 0.06 $\mu\text{g}/\text{m}^3$,

0.42 $\mu\text{g}/\text{m}^3$, 0.28 $\mu\text{g}/\text{m}^3$ 가

. HDI

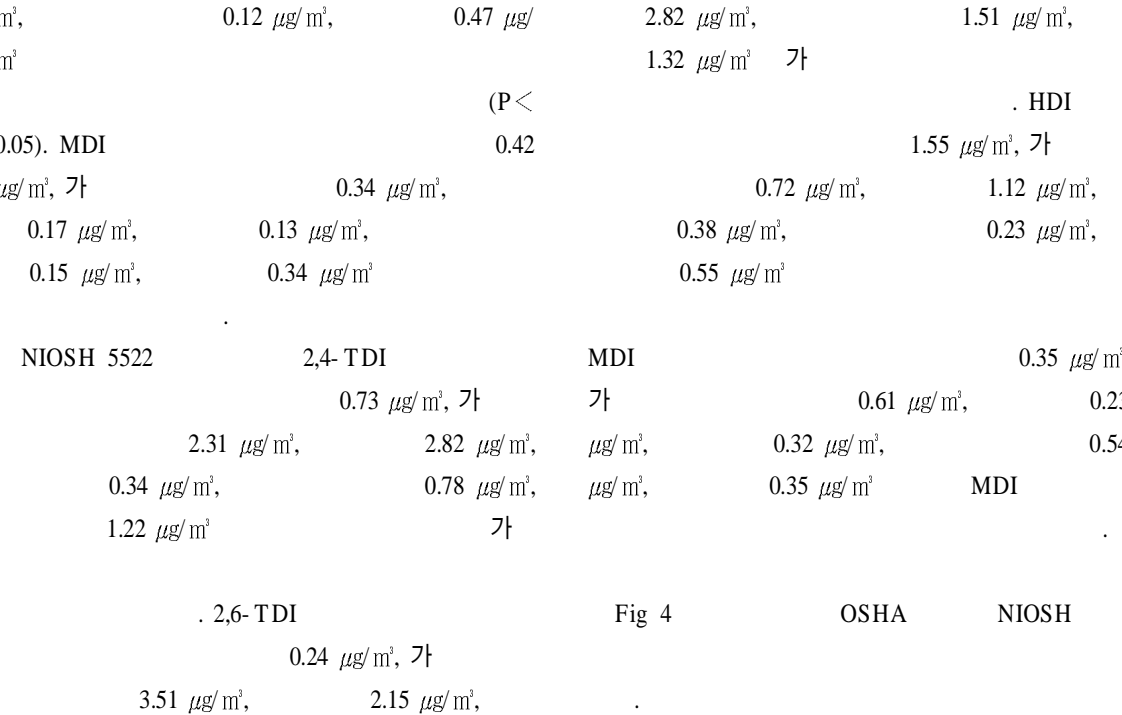
0.33 $\mu\text{g}/\text{m}^3$, 가

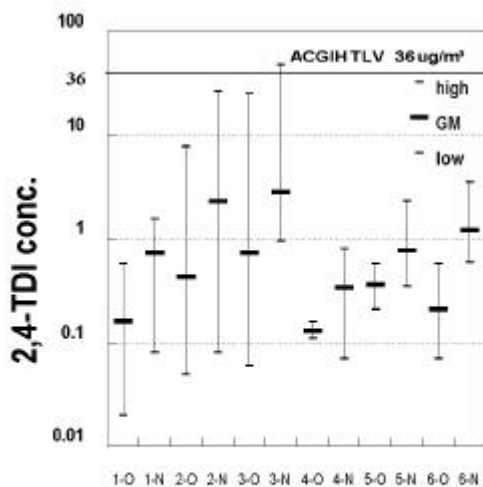
0.18 $\mu\text{g}/\text{m}^3$, 0.12 $\mu\text{g}/\text{m}^3$, 0.14 $\mu\text{g}/\text{m}^3$

Table 6. Comparison of isocyanates concentrations by each processes

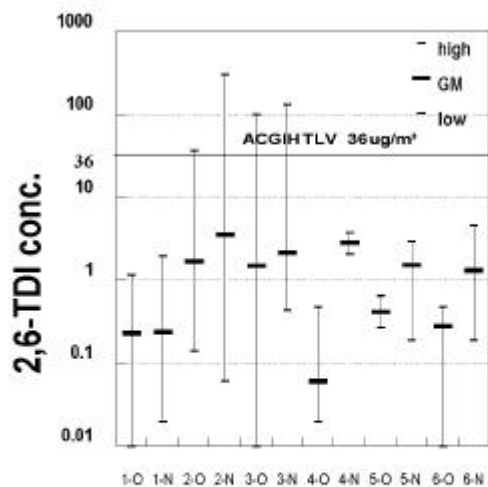
| Process | Method | N | Concentration ($\mu\text{g}/\text{m}^3$) | | | | | | | | | | | |
|--------------|--------|----|--|------|------------|----------|------|-------------|-------|------|------------|------|------|------------|
| | | | 2,4- TDI | | | 2,6- TDI | | | HDI | | | MDI | | |
| | | | GM | GSD | Range | GM | GSD | Range | GM | GSD | Range | GM | GSD | Range |
| Autobody SP | OSHA | 25 | 0.16 | 2.71 | 0.02- 0.58 | 0.23 | 4.91 | 0.01- 1.18 | 0.33# | 2.99 | 0.04- 2.57 | 0.42 | 1.31 | 0.14- 0.54 |
| | NIOSH | 25 | 0.73 | 1.99 | 0.08- 1.58 | 0.24 | 2.66 | 0.02- 1.95 | 1.55# | 2.29 | 0.02- 5.62 | 0.35 | 1.67 | 0.24- 1.78 |
| Furniture SP | OSHA | 34 | 0.43 | 3.64 | 0.05- 7.76 | 1.70# | 4.58 | 0.14- 37.15 | 0.18 | 2.31 | 0.02- 0.41 | 0.34 | 4.02 | 0.03- 36.3 |
| | NIOSH | 34 | 2.31# | 4.59 | 0.08- 26.9 | 3.51# | 7.82 | 0.06- 309.1 | 0.72 | 4.58 | 0.06- 79.9 | 0.61 | 6.53 | 0.05- 58.9 |
| Foaming | OSHA | 8 | 0.73# | 12.6 | 0.06- 25.1 | 1.48# | 23.9 | 0.01- 100.0 | 0.12 | 5.90 | 0.08- 0.63 | 0.17 | 2.97 | 0.04- 0.45 |
| | NIOSH | 8 | 2.82# | 3.60 | 0.96- 48.2 | 2.15 | 5.89 | 0.44- 131.8 | 1.12 | 3.89 | 0.20- 5.56 | 0.23 | 1.53 | 0.10- 0.45 |
| Mixing | OSHA | 3 | 0.13 | 1.20 | 0.11- 0.16 | 0.06 | 6.51 | 0.02- 0.48 | 0.14 | 4.65 | 0.02- 0.33 | 0.13 | 2.93 | 0.07- 0.45 |
| | NIOSH | 3 | 0.34 | 3.80 | 0.07- 0.81 | 2.82 | 1.35 | 2.04- 3.72 | 0.38 | 1.68 | 0.20- 0.50 | 0.32 | 1.50 | 0.21- 0.48 |
| UV coating | OSHA | 6 | 0.36 | 1.54 | 0.21- 0.58 | 0.42 | 1.48 | 0.27- 0.66 | 0.12 | 2.54 | 0.04- 0.33 | 0.15 | 2.73 | 0.07- 0.45 |
| | NIOSH | 6 | 0.78 | 1.95 | 0.35- 2.35 | 1.51 | 2.82 | 0.19- 2.95 | 0.23 | 1.40 | 0.20- 0.46 | 0.54 | 2.65 | 0.18- 2.29 |
| Adhesion | OSHA | 6 | 0.21 | 2.06 | 0.07- 0.58 | 0.28 | 4.02 | 0.01- 0.48 | 0.47# | 1.83 | 0.33- 1.35 | 0.34 | 2.14 | 0.06- 0.45 |
| | NIOSH | 6 | 1.22 | 2.02 | 0.60- 3.55 | 1.32 | 3.11 | 0.19- 4.57 | 0.55 | 3.25 | 0.19- 2.57 | 0.35 | 1.59 | 0.19- 0.60 |

Note : TDI=toluene diisocyanate; HDI=hexamethylene diisocyanate; MDI=methylene bisphenyl diisocyanate;
SP=spray painting; GM=geometric mean; GSD=geometric standard deviation; UV=ultraviolet;
N=number of samples;
; $p<0.05$ Duncan's multiple range test

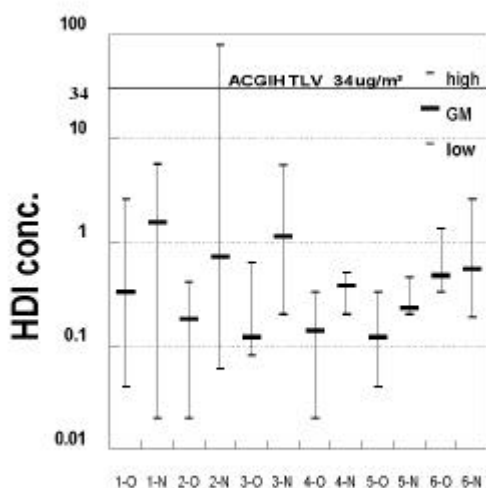




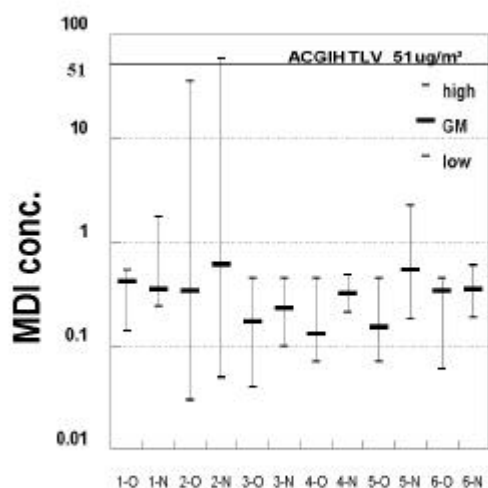
Process



Process



Process



Process

Fig. 4 Comparison of isocyanates concentrations by each process
 Process ; 1=autobody spray painting, 2=furniture spray painting, 3=polyurethane foaming,
 4=mixing, 5=UV coating, 6=urethane adhesion
 Conc. ; concentration, TDI ; toluene diisocyanate, MDI ; methylene bisphenyl diisocyanate,
 HDI ; hexamethylene diisocyanate, O ; OSHA method, N ; NIOSH method

3. (Woolich, 1982; Bardana Montanaro, 1992). Polymeric-based product

가 가 prepolymer oligomers
NIOSH
2,6- TDI, HDI 1 (Lesage
2,6- TDI MDI가 et al., 1992),
2 4 polyisocyanates가
가 . OSHA (Belin et al., 1981; Malo et al., 1983;
1 2,6- TDI가 . Nielsen et al., 1985).
NIOSH 1 가
2,4- TDI 2,6- TDI , OSHA 가
1 2,6- TDI가 (Janko et al., 1992; Vandenplas et al., 1992), HDI
prepolymer
(Vandenplas et al., 1993).
가
(. 1998a).

HPLC (Purnell et al., 1985;
C1/T1 + C2/T2 + C3/T3 + . . . + Cn/Tn Dharmarajan et al., 1987).
) C= ; T= N- (n- propyl)- N- (4- nitrobenzyl)- amine(Rando et al.,
1995), MPP(Bagon et al., 1984), 1- 2PP(Chang
Burg, 1982), TRYP(Wu et al., 1990),
9- methylaminomethylanthracene(Sangö Zimerson,
1980)
가 NIOSH
8 OSHA 1 가
“1” NIOSH
2 OSHA 1 가 “1”

가 NIOSH
8 OSHA 1 가
“1” NIOSH
2 OSHA 1 가 “1”

IV.

Swedish method 9- methylaminomethylanthracene
(Sangö Zimerson, 1980), HPLC
3% triethylamine phosph-
hate(pH 3) triethylamine
HPLC
Rudzinski (1996) 1- (9- anthracenylmethyl)
piperazine

methoxyphenylpiperazine, TRYP, 9- methyl pooled CV가 5% 가
aminomethylantracene Table 3, 4 HDI
NIOSH 5522 OSHA
가 (Rudzinski et al., 1996). 42
1- (9- anthracenylmethyl)piperazine (LOD) Table 5
2,4- TDI 8 , 2,6- TDI 3 , HDI MDI
가 1.6 OSHA 42 NIOSH 5522
가 . 가 NIOSH
가 5522 가
가 OSHA 42 ,
NIOSH 5522 ,
가 가 NIOSH 5522
가 .
OSHA 2,4- TDI
3 4 0.73 $\mu\text{g}/\text{m}^3$
2,6- TDI NIOSH 5522 가
가 , HDI OSHA 42 1.70 $\mu\text{g}/\text{m}^3$, 1.48 $\mu\text{g}/\text{m}^3$
가 (P<0.05). NIOSH 5522 (P<0.05). HDI
TRYP DMSO가
0.47 $\mu\text{g}/\text{m}^3$, 0.33 $\mu\text{g}/\text{m}^3$
(P<0.05). MDI
TRYP . NIOSH
2,4- TDI 가
TRYP NIOSH 5521 2.31 $\mu\text{g}/\text{m}^3$, 2.82 $\mu\text{g}/\text{m}^3$
MPP가 43mg 5522 2,6- TDI 가
TRYP가 450mg . HPLC 3.51 $\mu\text{g}/\text{m}^3$
TRYP가 (P<0.05). HDI
TRYP
HDI . , HDI 1.55 $\mu\text{g}/\text{m}^3$ (P
OSHA 42 <0.05). MDI
HDI polyisocyanate가
2,4- TDI 가
, 2,6- TDI
NIOSH 가 HDI가
HDI OSHA Rudzinski (1995, 1996)
(P<0.05). HDI polyisocyanate 1 mg/

m^3 ACGIH , ,
(Rudzinski et al., 1995; Rudzinski et al., 가 , 가
1996). TDI polyurethane flexible foam 25
가 11 , , ,
2,4- TDI 2,6- TDI가 , 1998 9
. Tinnerberg flexible foam 1998 10 OSHA
2,4- TDI $29.8 \mu\text{g}/\text{m}^3$ 42 NIOSH 5522
(Tinnerberg et al., 1997). 가
가 .
가 가
가 NIOSH 1. 2,6- TDI NIOSH
8 OSHA 1 가 “1” 5522 , HDI
, NIOSH 2 OSHA 42 .
OSHA 1 가 “1” . 2,4- TDI ,
. 2,6- TDI NIOSH
가 HDI
가 2,4- TDI, 2,6- TDI, HDI, OSHA .
MDI 가 . 2.
pooled CV가 5% 가 HDI
NIOSH 5522 OSHA
target 42 .
가 가 3. (LOD) 2,4- TDI, 2,6- TDI,
가 . HDI, MDI 8 , 3 , 1.6 , 1.5
, 가 NIOSH 5522 OSHA 42
chamber .
가 4. OSHA 42 2,4- TDI
 $0.73 \mu\text{g}/\text{m}^3$
가 . , 2,6- TDI 가
airbone chamber $1.70 \mu\text{g}/\text{m}^3$,
, $1.48 \mu\text{g}/\text{m}^3$
. HDI
가 . $0.47 \mu\text{g}/\text{m}^3$, $0.33 \mu\text{g}/\text{m}^3$
. MDI
V. . NIOSH 5522
2,4- TDI 가
OSHA 42 NIOSH 5522 $2.31 \mu\text{g}/\text{m}^3$, $2.82 \mu\text{g}/\text{m}^3$
4 4 , 2,6- TDI

는 가구 스프레이 도장 공정이 3.51 $\mu\text{g}/\text{m}^3$ 로 다른 공정에 비해 통계학적으로 유의하게 높았다. HDI의 경우는 자동차 스프레이 도장 공정이 다른 공정에 비해 1.55 $\mu\text{g}/\text{m}^3$ 로 통계학적으로 유의하게 높았다. MDI는 모든 공정간에 통계학적으로 유의한 차이는 없었다.

5. 공정별 이소시아네이트류 노출기준 평가는 복합물질에 대한 상가작용을 고려하여 평가한 결과 가구 스프레이 도장 공정의 NIOSH 방법의 시료 8개와 OSHA 방법의 시료 1개가 노출지수 “1”을 초과했고, 발포 공정의 경우 NIOSH 방법의 시료 2개와 OSHA 방법의 시료 1개가 “1”을 초과했다.

이상의 결과로 보아 NIOSH 5522 방법이 OSHA 42 방법보다 정확도, 정밀도 그리고 감도가 떨어지지 않았다. 또한 공기 중 이소시아네이트류에 대한 올바른 평가를 위해서는 단일물질의 평가보다는 혼합물질의 상가작용을 고려한 평가 방법이 바람직하다. 아울러 향후 공기 중 이소시아네이트류에 대한 평가는 단량체 보다는 비단량체 이소시아네이트류에 대한 측정평가 방법의 연구가 필요하다.

감사의 글

본 연구에 많은 조언을 해주신 가톨릭 대학교 예방의학교실의 노영만 교수님께 감사드립니다.

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