

9-Anthracenylmethyl 1-Piperazinecarboxylate(PAC)을 이용한 공기중 총이소시아네이트 분석방법 개발: 제1부 반응조건 및 안정성

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-Abstract-

Development of a New Method for Total Isocyanate Determination Using the Reagent 9-Anthracenylmethyl 1-Piperazinecarboxylate(PAC): Part 1 - The reaction condition and stability

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A new analytical procedure for the measurement of monomeric isocyanates and total isocyanate group in workplaces has been investigated. The method described here involves derivatization of the isocyanate sample upon collection with the reagent 9-anthracenylmethyl 1-piperazinecarboxylate (PAC). Laboratory investigations have demonstrated that excess PAC reagent can be satisfactorily removed from PAC-derivatized monomeric isocyanates—a requirement for the success of the analytical procedure. After removal of excess PAC reagent, the PAC derivatives of butyl isocyanate, phenyl isocyanate, HDI, MDI, and TDI were reacted with sodium thiomethoxide to convert them all to 9-anthracenylmethyl methyl sulfide (AMMS).

Total isocyanate group was determined by HPLC analysis and quantification of the single AMMS peak. This circumvents many of the disadvantages

associated with current HPLC methods. There were no longer problems associated with quantifying late-eluting peaks and analysis times were very short. A single detector was used for quantification because a standard of the analyte existed and the retention time could be determined. Because all species were converted to a single analyte, the problem of variability of response factors among different species was averted. Finally, there were no complex chromatograms to interpret. Monomers or other individual species were measured by analysis of the sample before the individual species were converted to AMMS. The favorable performance of PAC warrants its further study as a reagent for the determination of total isocyanate group in air.

Key words : isocyanate, total isocyanate, HPLC, PAC, TDI, MDI, HDI

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I . 1 mg/m³
(Tornling et al, 1990).
8 가 0.5 mg/m³ ,
1 mg/m³ .
(monomer) (Purnell and Walker, 1985;
Dharmarajan, 1987)
(Musk et al, 1988).
(NIOSH), (1957) Marcali
(OSHA)
가 (ACGIH)
가 5 ppb, (STEL) 가 . 1-(2-methoxyphenyl)
(Ceiling limit) 20 ppb piperazine
(NIOSH, 1978: NIOSH, 1992: OSHA, 1976:ACGIH, 가
1998). (HSE, 1987)
(oligomer)
(Vandenplas, 1992:Tornling, 1990: Silkt, 1983). (基) (number)
(Streicher, 1992)
tryptamine
가 가
(HPLC) 1-(2-
methoxyphenyl)piperazine
가 가 (Wu, 1990).
(HSE, 1987)
(group, NCO) (number) (基) HPLC
(HSE, 1987; Randol et al., 1996; Streicher
et al., 1996)
8 20 μg
NCO/m³ , 10 70 μg NCO/
m³ HPLC
5 ppb 20 ppb
OSHA NIOSH ACGIH
(Miles) 8 가 0.5 mg/m³

gradient
 가 가 가 가
 9- anthracenylmethyl
 1- piperazinecarboxylate(PAC)
 PAC- isocyanate sodium thiomethoxide
 9- anthracenylmethyl methyl
 sulfide(AMMS) (Fig.1). HPLC
 AMMS
 가 가 가 가
 가 가 HPLC
 가 가
 가 (Streicher, 1996). HPLC
 gradient

II.

1.

Burdick and Jackson
 (Baxter Healthcare Corp., Muskegon, Mich.)
 9- Anthracenemethanol(97%), p- nitrophenyl
 chloroformate(97%), N,N,- dimethylform amide
 (99.8%), sodium thiomethoxide(95%), phenyl
 isocyanate(98%), 1,6- hexamethylene diisocyanate
 [HDI](98%), phosphoric acid(99.999%), and silica
 gel (high- purity grade, 70- 230 mesh) Aldrich
 (Milwaukee, WI, USA)
 HPLC Toluene-2,4- diisocyanate [2,4- TDI] Sigma(St.Louis,
 MO, USA) 4,4'- Diphenylmethane
 diisocyanate [MDI] Kodak(Rochester, NY, USA)

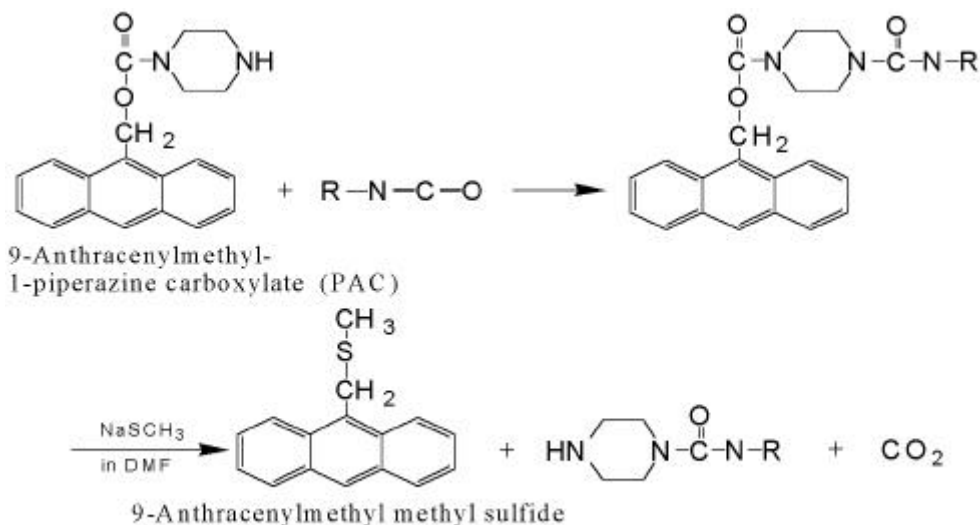


Fig. 1. How the PAC method works.

Butyl isocyanate Pfaltz and Bauer(Waterbury, CT, USA)
 Triethylamine (99.5%) Pierce (Rockford, IL, USA)
 solid-phase extraction (SPE) Supelclean LC Si(Supelco Inc., Bellefonte, PA, USA) 3 ml
 (TLC) EM Science(Silica gel 60 F254, 20 x 20 cm, Gibbstown, NJ, USA)
 (Waters, 717 Plus, USA), Nova-Pak C18 (150 x 3.9 mm, 4-um particle size, Millipore, Milford, MA, USA.)가
 HPLC(Waters Model M626, Millipore, Milford, MA, USA) 65% acetonitrile/35% 0.1 M triethylammonium phosphate pH 3.0
 (Waters 486 Tunable Absorbance Detector (Millipore, Milford, MA, USA) 254 nm, (ABI Analytical Spectroflow 980 Programmable Fluorescence Detector, Applied Biosystems, Ramsey, NJ, USA) 254 nm 425 nm

2. PAC

p-Nitrophenyl chloroformate(4.89 g, 24 mmole)
 100 mL tetrahydrofuran (THF)
 500- mL
 9- anthracenemethanol(3.36 g, 16.2 mmole)
 pyridine (2.56 g, 32.4 mmole) 가
 TLC
 THF
 p-nitrophenylchloroformate가 anthrylmethyl
 p-nitrophenyl carbonate . 40 mL DMF
 piperazine (14.0 g, 162 mmole)
 TLC
 45 가
 10% sodium carbonate 100 mL 100 mL 2

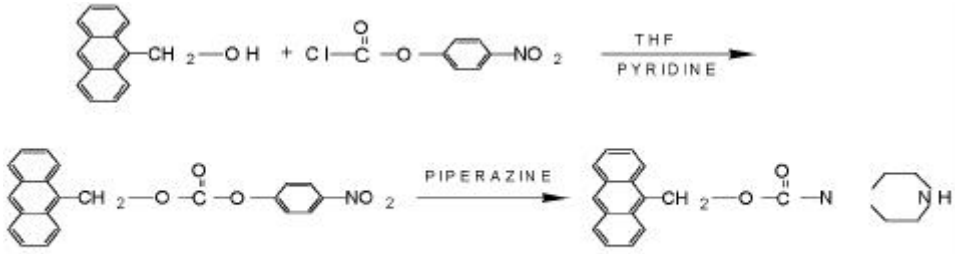


Fig. 2. Molecular structures showing synthesis of PAC.

1 M HCl 가

1.49 g / 22 mL
 1.35 g PAC (2:1)
 AMMS 88% (0.193 g)

(Fig.2)

5. PAC Isocyanate-PAC

3. PAC

PAC (0.63 g, 1.96 mmole) 35 mL

phenyl isocyanate (0.26 g, 2.2 mmole, 10% excess)

TLC 3, 2
 phenyl isocyanate-PAC(Ph-PAC) 0.81 g
 94% butyl isocyanate-PAC(Bu-PAC),
 HDI-PAC, 2,4-TDI-PAC, MDI-PAC
 Ph-PAC

PAC sodium
 thiomethoxide AMMS
 PAC
 Solid-phase extraction(SPE)
 PAC
 PAC Rf
 가 Rf TLC
 가

4. 9-Anthracenyl methyl Methyl Sulfi d (AMMS)

가 Sodium thiomethoxide
 (0.474 g, 6.76 mmole) 40 mL DMF
 가 Ph-PAC(0.404
 g, 0.92 mmole) 가 TLC
 60

HDI-PAC

6. Isocyanate-PAC

AMMS

Isocyanate-PAC

sodium thiomethoxie 가 TLC

DMF . 5% DMF 95%

TLC 가 HDI- PAC Rf가

0.47 , Ph- PAC Rf가 0.93

III. 가 PAC Rf가 0.03

1. HPLC Rf(PAC) Rf(isocyanate- PAC)

- PAC AMMS (Rf (isocyanate- PAC) / Rf (PAC))

acetoneitrile triethylammonium phosphate 가 isocyanate- PAC

(pH3.0) AMMS HPLC 31(Ph- PAC), 28(Bu- PAC), 27(MDI- PAC),

- PAC . 65% acetoneitrile 35% HDI- PAC

triethylammonium phosphate (pH3.0) 가 가

isoacynate- PAC Rf(HDI- PAC)/Rf(PAC)

AMMS DMF 6%

Rf 0.59 Rf(HDI- PAC)/Rf(PAC)

18 PAC

PAC SPE

HDI- PAC

HDI- PAC 101 % PAC

HDI- PAC

(Fig.3)

isocyanate- PAC AMMS

anthracene (基)

(基)

(Streicher et al., 1996;

Randol et al., 1995). anthracene (基)

254nm

가

2. PAC isocyanat e- PAC

PAC 가 isocyanate- PAC thiomethoxide가

3. Isocyanat e- PAC

100 mg/mL sodium thiomethoxide

Bu- PAC, Ph- PAC, HDI- PAC, TDI- PAC,

MDI- PAC AMMS

10 TLC

TLC isocyanate- PAC 가

10.6 ug/mL,

21.2 ug/mL, 42.4 ug/mL HDI- PAC

sodium thiomethoxide

110.7 %

sodium thiomethoxide

sodium

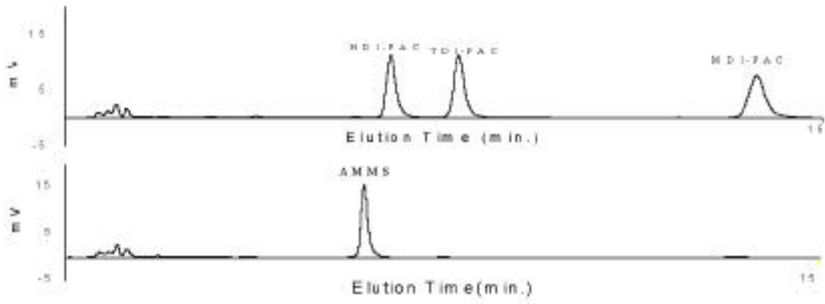


Fig. 3. HPLC analysis of PAC-monomer derivatives and 9-anthracenylmethyl methyl sulfide

sodium MDI가
 thiomethoxide 가 sodium thiomethoxide 가 (Fig. 4).
 100 mg/mL sodium PAC
 thiomethoxide 가 SPE PAC
 40 uL
 isocyanate-PAC 5. PAC :
 isocyanate-PAC AMMS가 isocyanate-PAC
 PAC sodium
 isocyanate-PAC 가 thiomethoxide AMMS
 가 SPE가 PAC
 AMMS
 4. PAC : PAC 가
 (基)
 PAC 가 0.1 mg

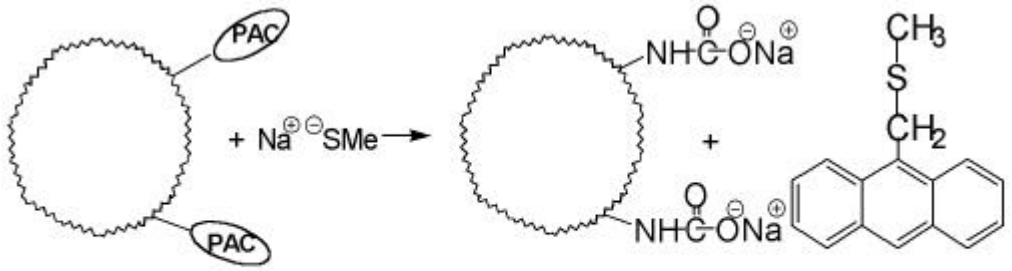


Fig. 4. Unique potential application of PAC:surface-bound isocyanate groups.

PAC
AMMS

0.044 %

PAC

blank level
가

가

PAC
가

가

가

HPLC

가

PAC

가

가

가

가

가

PAC

가

IV.

PAC

가

가

PAC

가

PAC

HPLC

가

PAC

PAC

butyl isocyanate, phenyl isocyanate,

HDI, MDI, TDI PAC 가 sodium thiomethoxide

AMMS

PAC

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