The effect of solvent selection in the gas chromatographic analysis of carbonyls in air samples after derivatization with pentafluorophenyl hydrazine

Md. Ahsan Ullah, Ki-Hyun Kim *, Jan E. Szulejko

Department of Civil and Environmental Engineering, Hanyang University, 222 Wangsimni-Ro, Seong Dong Gu, Seoul 133-791, Republic of Korea

A B S T R A C T

Carbonyl compounds are an important component of atmospheric chemistry with the potential to form secondary pollutants (in gaseous and/or particulate forms). For their analysis, derivatization by pentafluorophenyl hydrazine has been applied in gas chromatography (GC) or high performance liquid chromatography (HPLC). Because of the need for an appropriate solvent, we have evaluated the relative derivatization performance of five solvents (methanol, pentane, hexane, dichloromethane, and water) for GC analysis. Six light and common (C_1–C_5) aldehydes (i.e., formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, i-valeraldehyde, and valeraldehyde) out of a large member of carbonyl compounds were selected in this research. Anomalously large response was observed for the formaldehyde-hydrazone prepared in methanol and water, while that of acetaldehyde-hydrazone was reduced for pentane (by ~89%) relative to the others. If we exclude these biased cases, their response factors were in the order of: methanol > pentane > hexane > dichloromethane > water. This ordering was seen consistently in their relative recovery: methanol > pentane > dichloromethane ≈ hexane > water. The method detection limits (ng) of the aldehyde-hydrazone (as aldehyde mass) in each solvent were in the order: 1.0 (hexane) < 1.2 (dichloromethane) < 1.6 (methanol) < 2.5 (pentane) < 4.0 (water). As such, evidence suggests that solvent should be selected carefully to optimize the GC-based quantitation of aldehyde-pentafluorophenyl-hydrazones.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Low molecular weight carbonyl compounds (CC) are one of the major classes of volatile organic compounds worsening atmospheric air quality due to photochemical smog formation (Grosjean et al., 1983). CCs are the first intermediate species of photo-oxidation reaction of volatile organic compounds (VOC). They absorb solar radiation and produce OH radicals, ozone, and peroxyacetylnitrates to initiate the reactions leading to photochemical smog (Duan et al., 2008; Ortiz et al., 2006). Moreover, some CCs like formaldehyde and acetaldehyde are well-known for their potential carcinogenicity (Liebling et al., 1984; Okada et al., 2012).

Because of their high volatility and reactivity, the quantification of CCs generally involves derivatization steps to achieve satisfactory recovery and sensitivity. In practice, the use of solid phase extraction (SPE) such as silica cartridges coated with acidified 2,4-dinitrophenylhydrazine (DNPH) for the HPLC-based analysis has been the most common choice for the quantitative determination of airborne CCs (Pal and Kim, 2007). Such a combination has a number of proven advantages, e.g., high resolution, good sensitivity for short chained carbonyls, and simple matrix conditions (Herrington et al., 2006; Kleindienst et al., 1998). In such

applications, hydrazone analyte derivatives bound on the SPE are best extracted by an organic solvent for analysis. However, the reliability of DNPH-HPLC approach has been questioned due to significant experimental biases in extraction efficiency, especially for heavier CCs (Li et al., 2009; Saha et al., 2012). In an effort to find a more reliable approach for CC analysis, the use of pentafluorophenyl hydrazine (PFPH) as derivatization reagent for GC (or GC–MS) analysis has gained considerable attention since the initial report of Cecinato et al. (2001). The presence of five (phenyl) fluorine atoms in PFPH allows to increase thermal stability and volatility of the PFP-hydrazones relative to the DNP-hydrazones for GC-based analysis (Ho and Yu, 2004).

As the superior performance of PFPH has been confirmed, it was used preferably as a reliable derivatization reagent for the GC-based quantification of CCs (Ho and Yu, 2004; Li et al., 2009; Pang et al., 2011). Derivatization is commonly done in solvent(s) such as: acetonitrile, ethanol, ethyl acetate, methanol, 2-propanol, dichloromethane, hexane, pentane, and water (Cecinato et al., 2001; Culleré et al., 2006; Kim and Shin, 2011; Ma et al., 2011; Pang et al., 2013; Rivero and Topiwala, 2004). Despite the need for a proper solvent in preparing the hydrazones, the relative performance between different solvent types has scarcely been evaluated in that respect. Hence, we investigated the relative performance of different solvents used as derivatization media for the GC-based analysis. For comparative purpose, a total of

* Corresponding author. Tel.: +82 2 2220 2325; fax: +82 1945.
E-mail addresses: kkim61@hanyang.ac.kr, kkim61@nate.com (K.-H. Kim).

five solvents were selected from four different chemical classes such as 1] hydrocarbons (pentane and hexane), 2] alcohol (methanol), 3] chlorinated solvent (dichloromethane), and 4] inorganic solvent (water).

Despite much progress achieved in the analysis of airborne carbonyls, many uncertainties still remain with respect to which options should be used for the accurate analysis, e.g., from the selection of instrumentation to pretreatment methods — either GC or HPLC or whether to use derivatization or not? For each method selected, one needs to validate the reliability of such selection. In this research, we aimed to expand the reliability in the gas chromatographic determination of carbonyls in relation to the selection of solvent effects. To this end, a series of laboratory experiments have been carried out to explore the efficacy of five different solvent media in GC analysis of CC-PFPH derivatives. All comparative experiments were conducted with aldehyde-PFP-hydrazones prepared in five different solvents and analyzed via direct injection of liquid working standards into a GC equipped with a flame ionization detector (FID). The calibration results of aldehyde-PFP-hydrazones obtained using different solvents were then examined in terms of several factors including response factors (RF), relative recovery (RR), detection properties, precision, and solvent artifact. Thus, the results of our study are expected to offer an in-depth evaluation of aldehyde PFPH derivatization in relation to the efficacy of each solvent selected for the standard preparation.

2. Materials and methods

2.1. Materials and reagents

In this study, a total of six CCs were selected as the target compounds for comparative analysis. As shown in Table 1, their common names and the two letter acronyms (in parenthesis) used in this study are given as follows: 1) formaldehyde (FA), 2) acetaldehyde (AA), 3) propionaldehyde (PA), 4) butyraldehyde (BA), 5) i-valeraldehyde (IA), and 6) valeraldehyde (VA). To allow for proper evaluation of GC detection properties between different aldehydes, the calibration analysis of aldehyde-PFPH standards was conducted with the addition of ortho-xylene (o-X) as an internal standard (IS). The relative performance of different solvents was investigated to assess the optimum derivatization conditions for the aldehyde-PFP-hydrazones by comparing calibration results of their standards prepared in five types of solvent: 1) methanol (MeOH), 2) pentane (Pn),

3) hexane (Hx), 4) dichloromethane (DCM), and 5) water (W). Basic information of all reagents is summarized in Table 1. We purchased primary grade chemicals, AA and BA (99%), dichloromethane (99.8%), PA, IA, VA, and o-X (97%) from Sigma-Aldrich, USA. Three solvents methanol (100%), pentane (100%), and hexane (99.5%) were purchased from J.T. Baker, USA. PFPH (97%) was also from Sigma-Aldrich, UK and used as received without further purification. Deionized water solvent was obtained after purification of normal tap water by reverse osmosis process (Human power I+, Korea).

To facilitate the comparative analysis, we defined and classified our experimental scheme into two stages, I and II consisting of five experiments in all (Fig. 1). In the initial stage (stage I), PFPH solubility was determined in three solvents (pentane, hexane, and water). However, PFPH solubility in DCM and MeOH was not determined, as PFPH readily dissolved in those solvents. In stage II, PFPH solutions were prepared in five different solvents at similar concentrations (~7.5 mg/mL). Then, primary standard of the aldehydes (5 mg/mL) in each solvent was mixed with the PFPH in the same solvent in three molar equivalents (except water, two molar equivalents). Details of our experimental approaches including the preparation of standards and analytical setups are provided in Supplementary information as Sections 2.2 and 2.3.

3. Results and discussion

3.1. Comparison of pentafluorophenyl hydrazine solubility in three different solvents

As the first step to explore the relative performance of solvent media in the calibration of the aldehyde-PFP-hydrazones under similar derivatization conditions, we assessed the solubility of PFPH in two different solvent classes: two n-alkane hydrocarbons (Pn and Hx) and one inorganic solvent (W) in experiment stage I. Initially, we determined the solubility of PFPH into Pn, Hx, and W with the following procedure: 1] stepwise addition of small quantities of PFPH at a time, 2] frequent shaking using a sonicator, and 3] visual inspection of saturation point by naked eye. The solubility data obtained by visual inspection facilitated the detection of the saturation point to facilitate GC analysis.

The procedures involved in data acquisition and calculation of PFPH solubility for target solvents are summarized in Table 2S. Different amounts (10–80 mg) of PFPH powder were added into the different clear glass vials (absolute capacity 4.5 mL) containing fixed amount of

Table 1
Basic information of commonly used solvent and those selected for the investigation of the solvent effect in the analysis of CC-PFPH derivatives in this work.

Order	Reagent type	Full name	Short name	Chemical formula	CAS number	Reagent purity (%)	MW (g/mol)	Density (g/cm^3)	FID RRF[a]	Reference
1	Derivatizer	Pentafluorophenylhydrazine	PFPH	$C_6H_3F_5N_2$	828-73-9	97.00	198	1.69	0.31	
2	Solvent	Methanol	MeOH	CH_4O	67-56-1	100	32.0	0.79	–	This study, Hoshika and Muto (1978), Pang et al. (2013)
3		Ethanol	–	C_2H_6O	64-17-5	–	46.07	0.79	–	Chi et al. (2007), Pang et al. (2013)
4		n-Butanol	–	$C_4H_{10}O$	71-36-3	–	74.12	0.81	–	Pillai et al. (2009)
5		Ethyl acetate	–	$C_4H_8O_2$	141-78-6	–	88.11	0.90	–	Pang et al. (2013)
6		Pentane	Pn	C_5H_{12}	109-66-0	100	72.1	0.63	–	This study, Vidal et al. (1993)
7		Hexane	Hx	C_6H_{14}	110-54-3	99.5	86.2	0.65	–	This study, Li et al. (2009), Pang et al. (2013)
8		Acetonitrile	–	C_2H_3N	75-05-8	–	41.05	0.79	–	de Mendonça Ochs et al. (2015), Pang et al. (2013)
9		Dichloromethane	DCM	CH_2Cl_2	75-09-2	99.8	84.9	1.33	–	This study, Cecinato et al. (2001)
10		Water	W	H_2O	7732-18-5	100	18.0	1.00	–	This study, Rivero and Topiwala (2004)
11	Analyte	Formaldehyde	FA	HCHO	50-00-0	36.5–38	30.0	0.82	0.34	
12	(carbonyls)	Acetaldehyde	AA	C_2H_4O	75-07-0	99.0	44.1	0.78	0.38	
13		Propionaldehyde	PA	C_3H_6O	123-38-6	97.0	58.1	0.81	0.42	
14		Butyraldehyde	BA	C_4H_8O	123-72-8	99.0	72.1	0.80	0.45	
15		i-Valeraldehyde	IA	$C_5H_{10}O$	590-86-3	97.0	86.1	0.80	0.48	
16		Valeraldehyde	VA	$C_5H_{10}O$	110-62-3	97.0	86.1	0.81	0.48	
17	Reference	o-Xylene	o-X	C_8H_{10}	95-47-6	97.0	106.2	0.86	1.00	

[a] Predicted FID relative response factors (RRF) for aldehyde-hydrazones and PFPH referenced to o-X (RRF = 1.00). See text.