IDENTIFICATION AND QUANTITATIVE DETERMINATION OF HAZARDOUS NITROPHENOLIC COMPOUNDS IN THE EXHAUST GAS OF DIFFERENT KINDS OF DIESEL ENGINE BASED TRANSPORTATION VEHICLES IN HANOI CITY

Vu Duc Nam[1], Nguyen Thi Hanh[1], Pham Hung Viet [1], Yasuaki Maeda[2]

[1] *Centre of Environmental Technology and Sustainable Development (CETASD), Hanoi University of Science, Vietnam*

[2] *College of Engineering, Osaka Prefecture University, Japan*

ABSTRACT

In order to evaluate the status of air pollution caused by toxic organic compounds such as nitrophenols, numerous samples were taken in Hanoi city. The main purpose in this study was using absorption impinger system combined with an conventional liquid-liquid extraction method and gas chromatograph-mass spectrometry for analysis and evaluation for the trace of nitrophenols in exhaust gas of 13 typical different vehicle kinds using diesel fuel in Ha Noi City. These were 12 typical nitrophenol compounds estimated in this study. Concentrations of 2-nitrophenol and 4-nitrophenol were determined in the ranges of 22.47-489.15μg/m^3 and 18.27-628.90μg/m^3, respectively, depending on the loading capacity of each studied motor kind. Generally, concentration levels of mono nitrophenol compounds as 2-nitrophenol and 4-nitrophenol were found always higher than other nitrophenolic compounds. However, 2-Methyl-6-nitrophenol concentration found in the exhaust gas of derrick motor vehicle with 4.5 tons loading capacity seemed to be the highest (7066 μg/m^3).

Keywords: air pollutants, diesel engine, liquid-liquid extraction, nitrophenols, Vietnam

Introduction

Nitrated phenols are important organic pollutants in the atmosphere and known to be toxic to plants, aquatic organism and mammals. Nitroaromatic compounds are used as intermediates in the synthesis of pesticides and dyes, as well herbicides and insecticides, and especially nitrophenols can be formed in the atmosphere by photochemical reaction as hazardous air pollutants [(1) (2)]. Toluene, xylenes, phenols and methyl phenols (cresols) react in the gas phase with OH radicals and nitrogen oxides to form such hazardous nitrated phenols. Exhaust of diesel motors can be identified as major sources of nitrophenols in developing countries in the Southeast Asia [(3)]. Hanoi, capital city of Vietnam, is located in the northern part of the country with an area of 2146 sq km and the population of Hanoi is estimated about 3.5 millions peoples nowadays. Hanoi is the major transportation centre for the north, with roads providing links to all other major cities in Vietnam. Statistical data of year 2000 showed that total up to 5.10^5 different motor vehicles and 6.10^6 different motorbike vehicles are used in Vietnam. Among them, the motor vehicles used in Hanoi are appropriated 1/6 vehicles in whole Vietnam and are strongly increasing recently. However, there were still no studies in the past for investigation on determination of toxic organic compounds such as nitrophenols exhausted from motor vehicles using diesel fuel in Hanoi. Our study which was carried out at CETASD in the last 2 years showed that samples of exhausted gas from motor vehicles were absorbed in the alkali- impinge sampling system and extracted by continuous liquid-liquid extraction and analyzed for nitrophenols by using capillary gas chromatography coupled with mass spectrometry. An important target of this study was development of a simple and convenient analytical method in order to achieve reliable identification and accurate quantitation of trace of nitrated phenols in air.

Methods

Sampling and sample preparation

It is widely known that sampling and sample preparation can be contamination sources in environmental trace analysis. Analytes can be lost in the sample by adsorption to surfaces or by chemical transformation.

Other important source of quantitation errors is the contamination from the samples during collection and handing [4]. In order to avoid all these possible errors, the material for sampling device, the sampling procedure and the subsequent handing of the sample had to be controlled carefully. The engine of 13 different class cars (imported from Japan, Russia, Germany, and Korea). All motor operation settings, e.g. motor load capacity, exhaust gas temperatures were adjusted as standard parameters and performed on an electronic regulation console [5] [11] . After a warming time of about 15 minutes, the motor was operated constantly with the needed motor load. The sampling procedure of the exhaust gas was carried out after constant oil and exhaust temperature was reached.

The samples were taken about 30 cm after volume expansion with a sample probe made of stainless steel. The sampling system was described as bellow: The exhaust gas was trapped in a series of impingers, each of impinger was filled with 150 ml of the aqueous absorption solution. The impingers were immersed in an ice bath for stabilizing the solutes. Each motor kind was sampled three times for having average values. A flow rate of 1 litre per minutes was adjusted with a needle valve and a flow meter following with a membrane pump (MP-2N - SIBATA, Japan) was used. A gas drying device filled with blue gel was installed before the membrane pump in order to protect the pump from possible condensing moisture (dried test gas meter – SHINAGAWA, Japan). At the end of the sampling line a gas volume meter measured the sampled exhaust gas volume. Sampling time was half of an hour. This corresponds for undiluted exhaust gas volumes ranged about 30 litters. A total of 30 experiments were carried out within concentration of used absorption as 150 ml NaOH 1N solution (there were 13 investigated motor kinds and each motor kind was sampled duplicated or triplicated for having average values).

Twelve nitrophenols in samples of the exhaust gas could be identified in the impingers: 2-nitrophenol, 3-methyl-2-nitrophenol, 2-methyl-6-nitrophenol, 4-methyl-2-nitrophenol, 4-clo-2-nitrophenol, 4-methoxy-2-nitrophenol, 2,5-dinitrophenol, 2,4-dinitrophenol, 4-dinitrophenol, 3-methyl-4-nitrophenol, 6-methyl-2,4-dinitrophenol and 4-clo-3-nitrophenol.

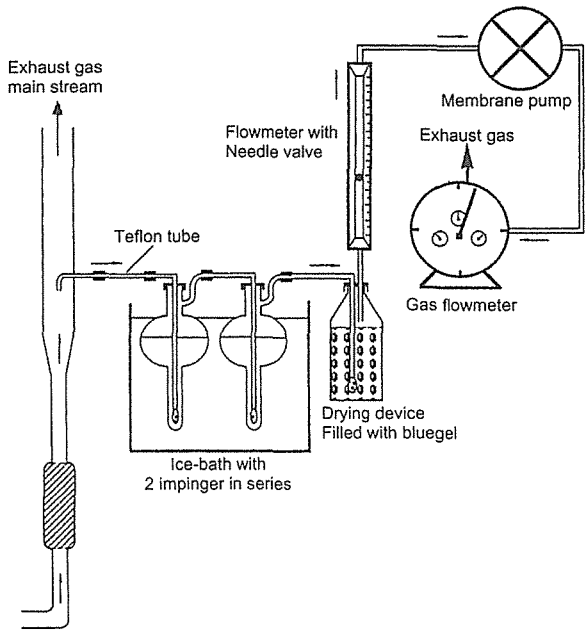

Fig. 1. Exhaust gas-sampling system

Table 1. List of 13 investigated motor vehicles as most popular in Hanoi City

No	Kind of motor	Abbreviation	Manufacture by	Vehicle load (tons)
1	CONGNONG	CN – 1	Vietnam	1.0
2	HYUNDAI	HD – 15	Korea	1.5
3	HYUNDAI	HD – 25	Korea	2.5
4	HYUNDAI	HD – 45	Korea	4.5
5	HYUNDAI	HD – 100	Korea	10.0
6	IFA	IFA – 50	German	5.0
7	KIA – RHINO	KIA – 50	Korea	5.0
8	KIA – RHINO	KIA – 14	Korea	1.4
9	KIA – RHINO	KIA - 40	Korea	4.0
10	PORTER	PT – 25	Korea	2.5
11	KAMAZ	KAMAZ - 100	Russia	10.0
12	ISUZU	ISUZU - 100	Japan	10.0
13	NISSAN (derrick)	NISSAN – 45	Japan	4.5

Sample treatment

The impinge solutions were prepared either on the day of sampling or the day before and kept it an ice bath until sampling. After sampling they were stored in the darkness in the air bath. Maximum storage time between sampling and extraction was 14 hours [6] [7].

Before extraction, pH of all samples was measured with a Metrohm pH meter. Sample solutions were added with 50 ml dichloromethane as pre-extracted procedure for other organic impurities and then remove the organic layer. After that, samples were adjusted to pH 2 ± 0.1 by using H_2SO_4. Under continuous mixing of the solution with Teflon covered magnetic stirrer, the internal standard (nitrocyclopentane) was added into solution. Samples were continuously extracted twice with each 50 ml dichloromethane for 4 hours and remove the aqueous layers. Subsequently, the organic layer was dried by anhydrous Na_2SO_4 and then concentrated on 60^{0}C water bath with rotary concentrator until 5 ml. Finally, samples were concentrated by N_2 stream that had been purified in prior with activated charcoal and then added with n-hexane up 1 ml before injected into GCMS [8].

Analytical conditions

All prepared samples were analyzed with a GCMS-QP5000 Shimadzu Gas Chromatograph equipped with Mass Detector. A 30m x 0.32 mm i.d. fused silica capillary column coated with a 0.25 μm film thinness of 5% Phenyl, 95% methylpolysiloxane (made by J&W Scientific) was used for the gas chromatographic separation. GC conditions were:

- Carrier gas : helium 99.999%,
- Column temperature program: 35^{0}C, after 2 minutes rising the oven temperature at a rate 3^{0}C/min to 70^{0}C and then increasing at a rate 8^{0}C/min to 250^{0}C, holding the column at the oven temperature of 250^{0}C for 5 minutes.
- Injector temperature: 250^{0}C
- Detector temperature: 280^{0}C
- Split ratio: 1/10
- Flow rate: 1.5 ml/minute

The mass spectrometer was operated as described below electron impact mode, positive ion detection mode, EM voltage 1.7 kV and selective ion monitoring (SIM mode).
For all target compounds, the molecular ions M^+ were chosen for SIM mode because they were the most abundant masses. Comparison of mass spectra and retention times with those of reference compounds was used for qualitative identification. Quantitation was conducted based on the comparison of integrated peak areas of molecular ions M^+ of the target compounds with those of the internal standards, respecting the obtained response factors from the analyses of a standard solution.

Recovery values for the sample preparation

For quantitative determination of nitrophenols in collected gas samples, recovery values were required to correct for the losses during sample preparation and analysis. The recovery values for whole procedure including sampling, sample preparation and analysis was determined as ratio of found amount of each nitrophenolic compound divided to a definitive known one of the corresponding after and before pushing the gas sampling system with 30 litters of a pure gas (e.g. nitrogen), respectively, assuming that the used gas contained no nitrophenolic compounds. The nitrophenol standard solutions were spiked in plastic bag containing 30 L of pure nitrogen gas. The nitrogen gas including nitrophenols was absorbed into the NaOH solution impingers as described in the sampling system above. The determined recovery values are given including the corresponding standard deviation expressed in percent to the mean values.

Results and discussion

Following the analytical results for studied nitrophenols in the 1st and 2nd impingers, the measured concentration for individual nitrophenols in the 2nd impinger was generally below 7% of the corresponding concentration in the 1st impinger. Therefore, there was no problem for the experiment with alkaline NaOH 1N solution; and for most samples, data correction for loss by breakthrough is not necessary since the overall error of sample treatment and analysis was in the same range. Moreover, the recoveries of the analytical method ranged of 85 % to 104 % (table 1). It is obvious that the analytical method applied was sufficient for quantitative trace determination of nitrophenols in exhaust gas.

Table 1: Recovery values of individual nitrophenols at each absorption impinge

No	Compounds		$H_{Impinger\ 1}$ (%)	$H_{Impinger\ 2}$ (%)	$H_{Impinger\ 1+2}$ (%)	Standard deviation (%)	Number of samples
1	2-nitrophenol	2-NP	89,75	2,85	92,60	5.2	3
2	3-methyl-2-nitrophenol	3-Me-2-NP	89,00	7,50	96,50	4.6	3
3	2-methyl-6-nitrophenol	2-Me-6-NP	92,50	5,56	98,06	4.2	3
4	4-methyl-2-nitrophenol	4-Me-2-NP	90,00	4,76	94,76	3.7	3
5	4-clo-2-nitrophenol	4-Cl-2-NP	83,50	7,68	91.06	5.6	3
6	4-methoxy-2-nitrophenol	4-MeO-2-NP	83,00	7,54	90.54	5.0	3
7	2,5-dinitrophenol	2,5-DNP	89,00	7,85	96,85	3.5	3
8	2,4-dinitrophenol	2,4-DNP	92,25	5,75	98,00	4.0	3
9	4-nitrophenol	4-NP	92,50	2,25	94,75	5.5	3
10	3-methyl-4-nitrophenol	3-Me-4-NP	93,75	2,15	98,99	5.0	3
11	6-methyl-2,4-dinitrophenol	6-Me-2,4-DNP	90,00	5,24	95,24	4.2	3
12	4-clo-3-nitrophenol	4-Cl-3-NP	92,54	5,45	97,99	5.3	3

Concentration of nitrophenols in exhaust gas of motor vehicles was calculated as below:

$$\text{Concentration } (\mu g/m^3) = \frac{\text{Concentration of calculated compound } (\mu g) * 1000\ (L/m^3)}{\text{V sample } (L) \times H_{Recovery}(\%)}$$

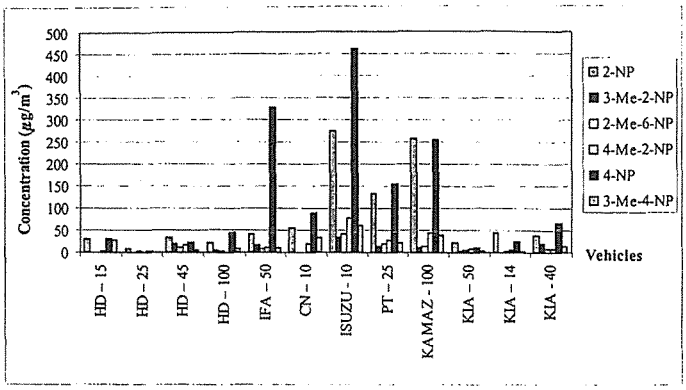

Fig. 2. Concentration of individual nitrophenols in exhaust gas of the investigated motor vehicles

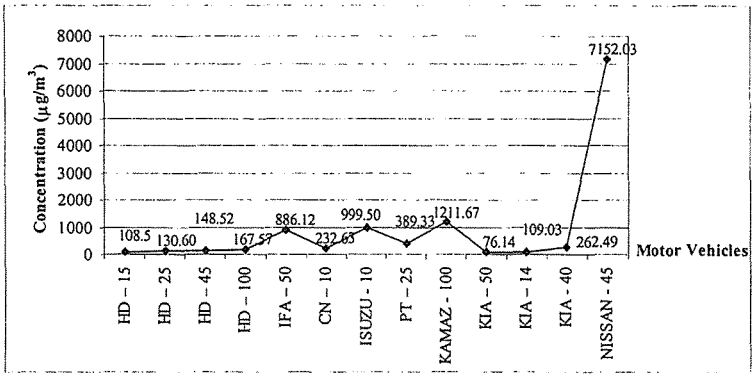

Fig. 3. Total concentration of nitrophenols in exhaust gas of 12 studied motor vehicles

Twelve nitrophenols could be identified for samples of the exhaust gas by comparison of their mass spectra and retention times with reference compounds, which had been analyzed with the same GCMS instrument conditions. For all investigated motor vehicles with motor load capacity between 1 - 10 tons, mainly found nitrophenol were presented in the concentration ranges such as 2-nitrophenol: 22.47 – 489.15 μg/m^3, 4-nitrophenol: 18.27 – 628.90 μg/m^3 and 3-methyl-4-nitrophenol: 3.02 – 78.09μg/m^3 depending on the studied motor load. Moreover, concentration of these nitrophenols present in the exhaust gas were very high for motor vehicles such as IFA 5 tons, CONGNONG 1 ton, POSTER 2.5 tons, KAMAZ 10 tons and ISUZU 10 tons. Concentration of 2,4-dinitrophenol and 6-methyl-2,4-dinitrophenol were absent for almost motor vehicles except that vehicle HYUNDAI 1.5 tons provided 0.23 μg/m^3 of these compounds in its exhaust gas.

For IFA, KAMAZ motors, concentration of nitrophenols was quite high. It could be explained that these kinds of motor were imported and used since 10 – 20 years ago so they were too old then when the vehicles are heavily loaded, diesel fuel were burned incompletely that why the exhaust gas contented a lot of toxic compounds such as hydrocarbons, CO as well as nitrophenols. Some motor vehicles imported from industrial developed countries with high technology of engine manufacturing industries as Korea and Japan, concentration of nitrophenols present in undiluted exhaust gas was significantly lower than motor vehicles produced in Russia and the former East Germany. However, concentration of 2-methyl-6-nitrophenol found in exhaust gas of NISAN 10 tons derrick motor was especially very high: 7066.67μg/m^3 exhaust gas. Based on the comparison of studied motor vehicles with different loading capacity (1.5 tons,

2.5 tons, 4.5 tons and 10 tons), we clearly observed that the increasing of the motor load created also a increasing of the total concentration of nitrophenols discharged in the ambient air environment.

Conclusions

Numerous exhausted gas samples were collected in Hanoi City. The samples were analyzed to assess the pollution level of toxic nitrophenols in exhaust gas of 13 different typical motor vehicles using diesel fuel in Hanoi City. Twelve nitrophenols were found and the obtained data in this study showed that mono- and di-nitrophenols were most popular available in the exhaust gas of almost investigated motor vehicles, especially the mono-nitrophenols such as 2-nitrophenol and 4-nitrophenol were found at high concentration. Therefore, it was ensured that these nitrophenol compounds were created by oxidation process due to the incomplete burning diesel fuel. The obtained result in this study was a preliminary investigation for hazardous organic compounds in exhaust gases from motor vehicles using diesel fuel. There is still no guideline for the threshold concentration of nitrophenols in exhaust gas of motor vehicles discharged into the air environment in Vietnam. Further monitoring should be conducted to better assess the source and human exposure to such hazardous organic compounds as by-products formed during the burning of fuel in engine of motor vehicles. Such studies will help the Vietnamese authorities in environmental management field to set-up suitable countermeasures to protect the air environment from pollution by hazardous organic pollutants caused by more and more intensive transportation activities.

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References

1. Crutzen, P. *The role of NO and NO_2 in the Chemistry of the troposphere and stratosphere.* Ann Rev 1
2. Danford, N Hogan, L. Parry, J.M. Amodified hypotonic treatment to measure mitotic aneuploidy in a chinese hamster primary cell line. *Environmental and Molecular Mutagenesis 5, 948 (1983).*
3. Nojima, K., Kawaguchi, A., Ohya, T., Kanno, S., Hirobe, M.: *Studies on photochemical reaction of air pollutants. X. Identification of nitrophenols in suspended particulates. Chem. Pharm. Bull. 31, 1047-1051 (1983).*
4. Ellis, H. V. Hagensen, J. H. Hodgson, J. R. Minor, J. L.; Hong, C. B.; Ellis, E. R.; Girvin, J. D.; Helton, D. O.; Herndon, B. L.; Lee, C. C. *Manmalian toxicity of munition compounds. Phase 3: Effect of life-time exposure. Part 1: 2,4- dinitrotoluene. Final Report No. 7, Project No 3900-B, Midwest Research Institute, Kansas City, MO. (1979).*
5. Salmon, R. J.; Buisson, J. P.; Hendrickx, B.; Vielh, P.; Aussepe, L.; Moens, W.; Royer, R. *In-vivo carcinogenicity of 2-nitro-oxaphenalenes. Carcinogenesis 10 (5), 803-805 (1989).*
6. Keith, L. H., Telliard, W. A. *Priority pollutants. I-a perspective view Environ. Sci. Technol. 13. 416-423 (1979).*
7. Spiegelhalder, B.; Preußmann, R. *Nitrosamines measurements in ambient air of an industrial area in Austria. IARC Scientific Publication No. 48 Anonymous 411(1987).*
8. Shea, P. J, Weber. J. B., Overcash M R.: *Biological activities of 2,4-dinitrophenol in plant-soil systems. Residue Reviews 87, 1-41 (1983).*
9. Gery, M. W., Fox, D. L., Jeffries, H. E., Stockburger, L., Weathers, W. S. A. *Continuous stirred tank reactor investigation of the gas phase reaction of hydroxyl radicals and toluene. Int. J. Chem. Kin 17, 931-955 (1985).*
10. Lies, K-H., Schulze, J., Winneke, M., Kraft, J., Hartung, A., Postulka, A., Gring, H., Schröter,D.: *Nicht limitierte Automobil-Abgaskomponenten. Volkswagen AG, D-3180 Wolfsburg (1988).*
11. Sosef Tremp, *Source and fate on nitrate phenols in the atmosphere environment, Doctoral natural sciences, Swiss federal institute of technology (EAWAG), 1992*