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International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

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To cite this Article De Andrade, J. B. , Pinheiro, H. L. C. and Andrade, M. V.(1993) 'Determination Of Formaldehyde And Acetaldehyde Associated To Atmospheric Aerosols By HPLC', International Journal of Environmental Analytical Chemistry, 52: 1, 49 — 56

To link to this Article: DOI: 10.1080/03067319308042847

URL: <http://dx.doi.org/10.1080/03067319308042847>

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DETERMINATION OF FORMALDEHYDE AND ACETALDEHYDE ASSOCIATED TO ATMOSPHERIC AEROSOLS BY HPLC

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(Received, 15 June 1992; in final form, 15 March 1993)

A rapid new analytical protocol was developed for the determination of formaldehyde and acetaldehyde associated to atmospheric particulate matter, at ng/m^3 levels. The aerosols were collected on glass fiber filters ($8'' \times 10''$) at face velocities ranging from 15 m/min to 23 m/min. Aliquots of 15.4 cm^2 were sonicated, for 20 min, with 5.0 mL of 0.01% 2,4-dinitrophenylhydrazine (DNPH), 1 % phosphoric acid. The liquid phase was then filtered and the separation and quantification of the corresponding 2,4-dinitrophenylhydrazone (DNPHo) derivatives carried out by reverse phase HPLC. Acetonitrile:water (57:43, v/v) as mobile phase at 1.0 mL/min and absorbance detection at 350 nm and 365 nm for, respectively, formaldehyde-DNPHo (0.04 AUFS) and acetaldehyde-DNPHo (0.01 AUFS) were used. The precision for four different aliquots, from a $8'' \times 10''$ glass fiber filter, were under 0.04% for formaldehyde and 14.16 % for acetaldehyde. In Salvador, Bahia, Brazil, formaldehyde and acetaldehyde were determined, respectively, in the range of 6.8 ng/m^3 to 27.3 ng/m^3 and 9.1 ng/m^3 to 54.6 ng/m^3 .

KEY WORDS: Atmospheric aerosols, formaldehyde, acetaldehyde, carbonyl compounds, HPLC.

INTRODUCTION

Aldehyde sources in the atmosphere include primary emissions from industrial plants, incinerators and automobiles, as well as secondary ones via photo-oxidation of methane, isoprene, and other biogenic and anthropogenic hydrocarbons^{1,2}. Concentrations of formaldehyde and acetaldehyde in the atmosphere are of great significance to atmospheric chemistry due to the strong influence these species have on photochemical smog processes³.

In the past decade a substantial amount of information on surface atmospheric levels of formaldehyde and acetaldehyde has been generated (see, for example, references 3–9). However, most of the knowledge about formaldehyde and principally of acetaldehyde in the atmosphere comes from measurements of the gas phase. Because carbonyl compounds are polar they can easily interact with particles of condensed matter, be adsorbed on soots, or dissolved in rain and fog⁷. In this way, data on aldehydes associated to atmospheric aerosols are needed for a complete description of the aldehyde budget in the atmosphere¹⁰. On the other hand, formaldehyde is currently regulated for its carcinogenic properties¹ and the overall risk associated with population exposure could be enhanced depending on the

concentration level and the particle size of the atmospheric aerosol which this compound is associated to.

In the present work we report a new and rapid analytical protocol for determining formaldehyde and acetaldehyde associated to atmospheric particulate matter, at ng/m^3 levels.

EXPERIMENTAL

Reagents and materials

All organic solvents used were chromatography grade (Merck) and were further redistilled with DNPH. DNPHo standards were precipitated using chromatographic grade DNPH, recrystallized twice following a method described elsewhere¹¹. The hydrazone standards were dissolved in acetonitrile.

Reagent preparation

The DNPH solution was prepared by diluting 20 mL of concentrated DNPH solution (100 mg/ 100 mL, in a solution of 1 % H_3PO_4 -acetonitrile by volume) with 2.0 L of deionized water 1% H_3PO_4 . The solution was then purified by three successive extractions with CCl_4 ¹². The DNPH solution was stored in a 2.5 L glass bottle containing 200 mL of CCl_4 and a teflon coated magnetic stirring bar.

Apparatus

A Varian liquid chromatograph (model 2510) equipped with a Rheodyne injector and a variable UV/VIS detector (model 2550) was used. In order to obtain the lower detection limit the wavelength and detector sensitivity were selected for formaldehyde and acetaldehyde, respectively, at 350 nm (0.04 AUFS) and 365 nm (0.01 AUFS). The analytical column used was Econosphere C18 5 μm , 250 mm \times 4.6 mm i.d. (Alltech). The mobile phase was acetonitrile:water (57:43 v/v) at 1.0 mL/min. In all cases 10 μL aliquots were used in the analysis.

Ultrasound bath Microsonic (model SX 10) and High volume sampler (Energética Ind. Com. Brazil) equipped with glass fiber filter -8" \times 10"- (Energética Ind. Com. Brazil) or quartz fiber filter -8" \times 10"- (Pallflex, 2500QAO-UP, USA), were used.

Sampling and analytical procedure

High volume samplers were employed to collect atmospheric aerosol on glass fiber filters, at face velocities ranging from 15 m/min to 23 m/min. The filters were previously weighted,

wrapped in aluminum foil and stored inside plastic bags, under refrigeration. After sampling the filters were weighted again and stored in the way described before.

The samples were collected at a bus station in Salvador, BA, Brazil, which corresponds to an area of ca. 13,920 m². The predominant traffic is diesel fueled buses which could arise the rate of 150 bus/hour in rush time. During four days one hour samples, from 8 am to 9 pm, were collected. During the collection period the temperature varied between 27°C and 30°C.

Aliquots of 15.4 cm² from the 8" × 10" glass fiber filters were reacted with 5.0 mL of aqueous solution 0,01 % DNPH (1% phosphoric acid), for 20 min, under sonication. The liquid phase was then filtered and injected directly into the HPLC system.

RESULTS AND DISCUSSION

Blank levels

The detection limit that an analytical procedure may achieve greatly depends on the reagent blank quality. Unlike successive recrystallization the DNPH showed contamination with formaldehyde and acetaldehyde DNPHo. Since hydrazones have much higher solubilities in non polar solvents such as CCl₄ than in aqueous phase^{12,13}, we prepared the DNPH solution in aqueous solution. It was purified by three successive extractions with CCl₄ and stored inside a glass bottle containing CCl₄. Before the use, the solution and CCl₄ were stirred vigorously for 10 min (fourth extraction). In Figure 1 it can be observed that the concentration levels of formaldehyde and acetaldehyde DNPHo, drop to 53 pmol and 11 pmol, respectively. Thus, resulting in a detection limit of the HPLC method (S/N=3 based on peak height) around 159 pmol and 33 pmol, for formaldehyde and acetaldehyde, respectively.

Another important aspect related to the blank level is the contamination of the filters used to collect the atmospheric aerosols. In Table 1 the levels of formaldehyde and acetaldehyde in the reagent DNPH, glass fiber filter (Energética Ind. Com. Brazil) and quartz fiber filter (Pallflex 2500QAO-UP, USA) are shown. It can be observed that the aldehyde levels in glass fiber filters are comparable with the reagent DNPH. However, the aldehyde levels in quartz fiber filters were much higher than the reagent DNPH, even after the extraction with acetonitrile and heating inside an oven or with a flame of a Bunsen's burner. In this way, all samples were collected using glass fiber filters.

Effect of ultra sonication on the derivatization reaction

The reaction between DNPH solution and aldehydes associated to atmospheric aerosols, behaves like a conversion "reagent to products" in an heterogeneous porous system, which involves mass transport of the reagents on the interface fluid-solid and in the inner sites of the particles¹⁴. In order to improve the mass transport during the derivatization reaction we used sonication on it. In Figure 2 it could be observed that the highest values of concentration

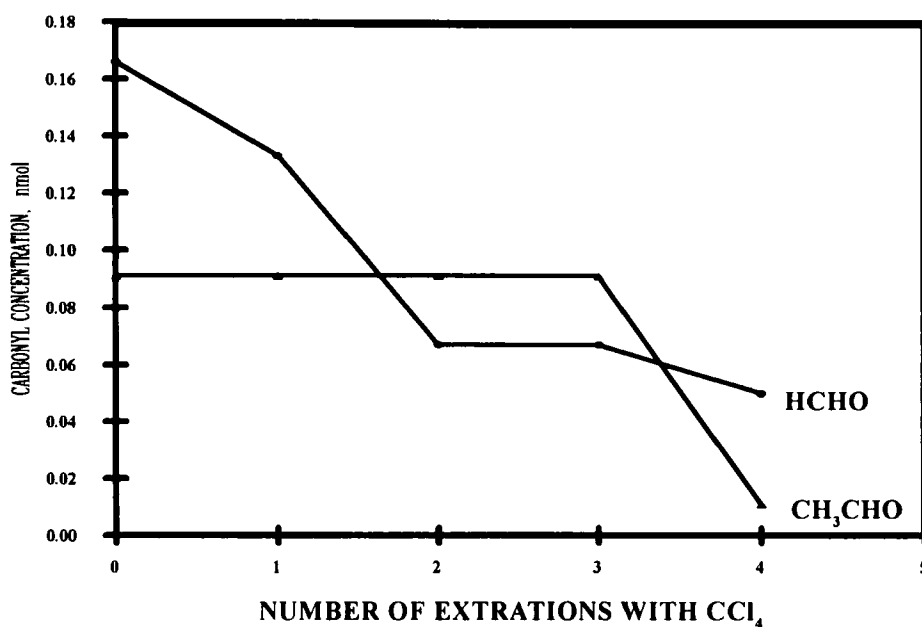


Figure 1 Extraction efficiencies of DNPHo of formaldehyde (HCHO) and acetaldehyde (CH₃CHO) with CCl₄ from the DNPH aqueous solution.

of formaldehyde and acetaldehyde were obtained when the derivatization reaction was carried out under sonication (20 min). These values did not change even for 4 hours after the sonication has been stopped. Meanwhile, the derivatization reaction without sonication (Figure 2) showed stable values for formaldehyde 20 min after the reagent mixing. However, for acetaldehyde it lasted ca. 1 hour to stabilize. For these reasons sonication was used in all aldehyde determinations throughout this study.

Table 1 Study of the blank levels of formaldehyde and acetaldehyde on glass fiber filters (GFF) and quartz fiber filters (QFF)*.

Filter type	Formaldehyde (pmol)	acetaldehyde (pmol)
DNPH solution	53	11
GFF	67	68
QFF	666	454
QFF after clean up	276 ^a 366 ^b	198 ^a 136 ^b

*Aliquots of 15.4 cm² reacted, under sonication, with 5 mL of purified DNPH aqueous solution.

^aThe filters were extracted with 5 mL of acetonitrile, under sonication, and heated inside an oven at 400°C for 24 h.

^bThe filters were heated with a flame of a Bunsen's burner for 10 min.

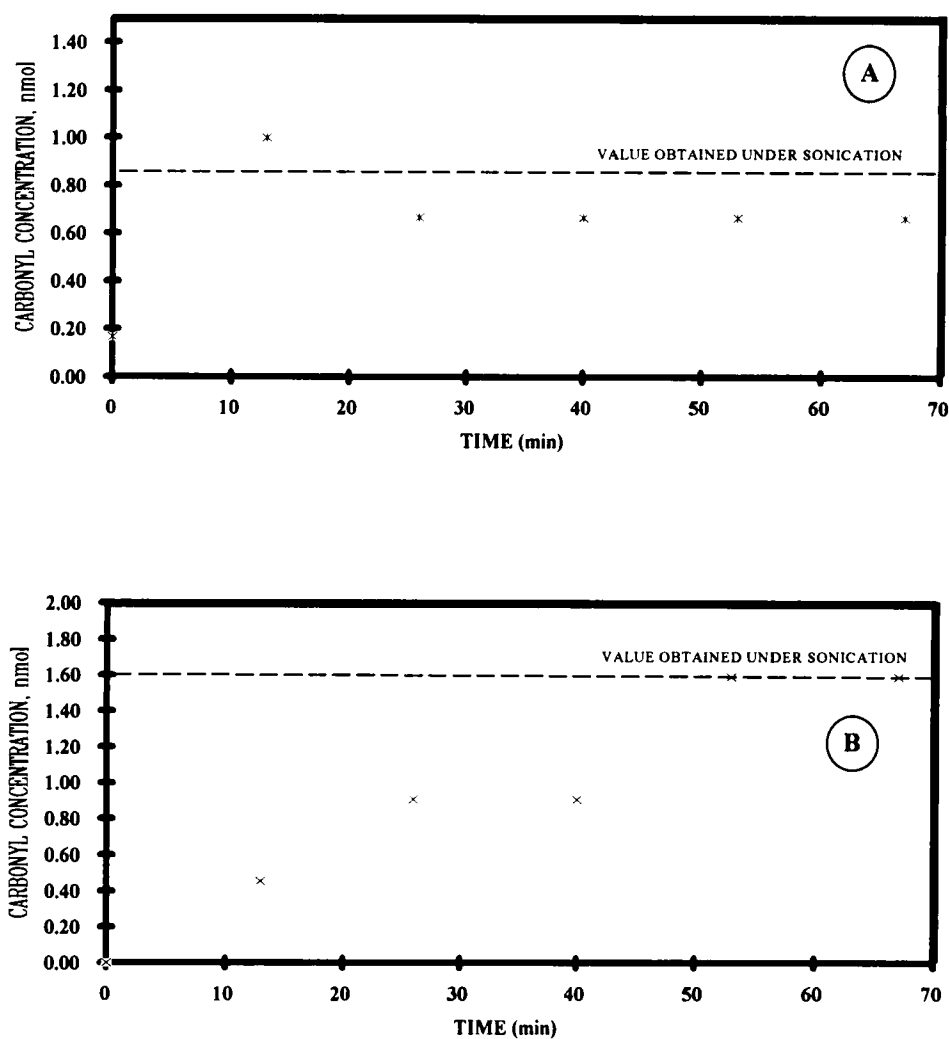


Figure 2 Rate of reaction between DNPH and formaldehyde (A) and acetaldehyde (B) associated to atmospheric aerosols.

A precision study in the determination of formaldehyde and acetaldehyde, in four different aliquots (15.4 cm^2) from a $8'' \times 10''$ glass fiber filter, is shown in Table 2. It can be observed that formaldehyde and acetaldehyde were determined with an average standard deviation of less than 1% and 15%, respectively.

Table 2 Precision study in the determination of formaldehyde and acetaldehyde, associated to atmospheric aerosols, in four different aliquots of an 8"×10" loaded glass fiber filter.

<i>Aliquot</i>	<i>Formaldehyde (ng/m³)</i>	<i>Acetaldehyde (ng/m³)</i>
1	13.63	34.38
2	13.64	34.38
3	13.63	27.26
4	13.63	38.79
average	13.63	33.70
r.s.d.	0.4%	14.1%

r.s.d. = relative standard deviation

Ambient levels of formaldehyde and acetaldehyde associated to the particulate phase

Ambient concentrations of formaldehyde and acetaldehyde in the site studied are listed in the Table 3. During the sampling period the formaldehyde and acetaldehyde concentrations ranged from 6.8 ng/m³ to 27.3 ng/m³ and 9.1 ng/m³ to 54.6 ng/m³, respectively. These values are smaller than those measured in gas phase in this place, which were from 24,2 µg/m³ to 58.1 µg/m³ for formaldehyde and 4.9 µg/m³ to 9.4 µg/m³ for acetaldehyde¹⁵. It can be observed that in the vapor-phase the major aldehyde was formaldehyde, whereas in particulate-phase, acetaldehyde prevails. Formaldehyde is known to form adducts or condensation products with many substances, both organic and inorganic, one of the most important being with SO₂, producing hidroxymethanesulfonic acid¹⁶. When formaldehyde is in this form it does not react with DNPH solution. This may explain the lower values for formaldehyde, in particulate-phase, when compared to acetaldehyde, whereas the corresponding adduct with acetaldehyde is not stable as that with formaldehyde¹⁶.

Table 3 Formaldehyde and acetaldehyde concentrations, particulate phase (ng/m³).

<i>date (1991)</i>	<i>sampling time</i>	<i>volume sampled (m³)</i>	<i>flow rate (m³/h)</i>	<i>formal- dehyde</i>	<i>acetal- dehyde</i>
03/04	11:24–14:24	198	1.10	13.63	40.90
	14:33–17:33	198	1.10	13.64	34.12
	17:40–20:32	188	1.09	21.62	50.44
	20:38–22:38	99	1.10	27.32	54.64
04/04	09:06–12:06	198	1.10	6.85	27.38
	12:12–15:12	198	1.10	6.82	27.27
	15:20–18:20	197	1.10	13.75	34.38
05/04	08:26–11:26	198	1.10	13.69	41.08
	11:35–14:05	167	1.11	8.15	32.60
	14:16–17:16	195	1.08	6.97	27.90
09/04	09:57–12:57	196	1.09	19.77	34.42
	13:30–16:40	209	1.10	12.93	38.79
	16:46–19:46	198	1.10	16.64	34.11

The particulate-phase/gas-phase concentration ratios, for both carbonyl compounds, are lower than 10^{-2} , so that more than 99% of the total aldehyde mass concentration is found in the gas-phase and less than 1% in the aerosol-phase. This is in agreement with previous data obtained by Klippel and Warneck¹⁰ and Grosjean⁴.

These small aerosol-phase concentrations appear to be much higher than those predicted on the basis of a simple equilibrium between aqueous and gas-phases^{4,10}. In this way, we believe that sampling artifacts may occur during filter sampling of ambient air when (for example) gaseous carbonyl compounds are adsorbed on the layer of deposited particulate matter⁴. A sampling protocol which minimizes the sampling artifacts is under investigation in our laboratory, involving the use of annular denuders coated with DNPH, followed by a filter, for the aerosol collection.

CONCLUSIONS

The results presented above show that reaction of the aerosol samples with purified DNPH aqueous solution, under sonication, and injection into HPLC system allows, without any pretreatment, the determination of formaldehyde and acetaldehyde, in low concentration levels with high precision.

Acknowledgements

This work was supported by the National Research Council of Brazil (CNPQ). The authors thank Mauro Korn, André Esteves, Fátima Justo, Anselmo Elcana and José Oscar N. Reis for useful discussions. H.L.C.P. is supported by a CAPES fellowship and M.V.A. is supported by a CNPq fellowship and is a faculty member at Universidade do Estado da Bahia (UNEB).

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