



DETERMINATION OF ALDEHYDES IN WET DEPOSITION

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Abstract: The paper presents two sample preparation procedures for the determination of aldehydes in wet deposition. In both cases the 2,4-dinitrophenylhydrazine derivatization and solid phase extraction were applied. The derivatization in method A was applied before the extraction, the extraction in method B was carried out with simultaneous derivatisation. Accuracy of both methods was evaluated on the basis of the analysis of aqueous solutions of selected carbonyl compounds. Both methods were characterized by good recovery, however, due to the precision of the method expressed as RSD for testing of environmental samples the method B was used.

The analysis of environmental samples showed significant differences in the concentrations of aldehydes in wet deposition, depending on the location of the sampling point. In the case of samples taken from agricultural areas the predominant aldehydes were formaldehyde and acetaldehyde. Formaldehyde was from 31% to 47% of the determined compounds. While in samples collected near a traffic source, in the deposition acrolein was determined at the levels from 62% to 64% of the identified compounds.

INTRODUCTION

Aldehydes present in the atmosphere come from natural and anthropogenic sources. Natural sources of aldehydes are mainly the reactions occurring in the troposphere, which are the primary contaminants. By the process of photochemical oxidation reactive hydrocarbons are transformed into aldehydes [7]. Aldehydes are also potential compounds which in the atmosphere can undergo further transformations as a result of which secondary organic aerosols [23] are formed. The main anthropogenic source of formaldehyde and acetaldehyde are industrial processes and emissions [1]. In the ambient air, aldehydes occur at a level of several $\mu\text{g m}^{-3}$ [2, 18], while in wet deposition, depending on the compound, the concentration level is of a few dozen to more than 1 000 $\mu\text{g dm}^{-3}$ [11, 16, 24]. The concentration of aldehydes in the air is depending on the time of day, season, concentrations of O_3 , HNO_3 and organic aerosols.

Most methods for determination of aldehydes in environmental samples are based on separation techniques, such as gas or liquid chromatography and electrophoresis. In most cases, due to the physicochemical properties of this group of compounds, analytical procedures include derivatization step. Frequently used as a derivatization reagents are such derivatives of hydrazine as: 2,4-dinitrophenylhydrazine (DNPH) [5, 12, 17, 21], 2,4,6-trichlorophenylhydrazine (TCPH) [20], 2,3,4,5,6-pentafluorophenylhydrazine (PFPH) [14], 5-(dimethylamino)-naphthalene-1-sulfon-hydrazide (DNSH) [19], 3-methylbenzothiazole-2-hydrazine (MBTH) [11], 4-(N,N-dimethylaminosulfonyl)-7-N-methylhydrazino-2,1,3-benzoxadiazole (MDBDH) [9], 5-amino-4-sulfanylphthalhydrazide (ASPH) [8], hydroxylamine derivatives (O-benzylhydroxylamine (BOA) [10], *o*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) [15], Hantzsch reagents (1,3-cykloheksadion (CHD), 5,5-dimethyl-1,3-cykloheksadion (Dimedon), 4-amino-3-penten-2-one (Fluoral P), acetylacetone, acetoacetanilid or 2-aminoethanethiol (cysteamine), 3-amonofluoroethan [6, 22]. DNPH is the commonly used derivatization agent for high performance liquid chromatography (HPLC), whereas PFBHA is usually used for gas chromatography. U.S. Environmental Protection Agency (EPA) in the analytical procedure for determining aldehydes in the air recommends use of DNPH for determination of aldehydes by HPLC [5] and PFBHA for gas chromatography (GC). Hantzsch reagents, which react with aldehydes to form fluorescent compounds, are normally used in the injection – flow analysis [6].

In the analysis of water and wet deposition samples, derivatization step is preceded by analytes enrichment methods as a solid phase extraction (SPE) or solid phase microextraction (SPME), in some cases derivatization is carried out on the bed of sorbent. The authors [3, 4, 26] extracted 2,4-diphenylhydrazine derivatives of aldehydes with solid phase extraction, using the SPE columns with octadecyl groups (C18). The concentrated sample was then analyzed by HPLC chromatography. Tsai and Chang [25] proposed the determination of aldehydes in water samples using gas chromatography coupled with mass spectrometry. Before the analysis, the sample was preliminary prepared, by headspace microextraction to the stationary phase and derivatized on the fiber coated with poly (dimethylsiloxane)/divinylbenzene (PDMS/DVB).

This paper presents a comparison of methods for the determination of aldehydes in samples of wet deposition using derivatization with 2,4-DNPH before and during the SPE operation. Quantitative determination of derivatives of aldehydes was performed by high performance liquid chromatography coupled with diode array detector (HPLC/DAD). For each of the methods LOD, LOQ, RSD and the recovery of the analyte were determined.

In the present study, seven low-molecular weight aldehydes, including formaldehyde, acetaldehyde, acrolein, propionaldehyde, crotonaldehyde, N-butyraldehyde, benzaldehyde were measured in wet deposition at agricultural and urban sites.

EXPERIMENTAL

Materials and equipment

The analytical system consisted of an isocratic pump (model Perkin Elmer series 200), connected to a DAD detector adjusted at 360 nm. Separation was achieved on a Spheri-10 RP-18 column (10 μ m, 250 \times 4.6 mm) (Perkin Elmer, USA). The mobile phase was 60:40 acetonitrile-water flowing at 1.5 mL min⁻¹. Samples were injected by a Rheodyne

valve equipped with a 10 μL loop. HPLC calibration was performed with standard solutions TO11/IP-6A Aldehyde/Ketone-DNPH Mix (Supelco Analytical, USA). The concentrations of hydrazones in standard solution are given in Table 1. The chromatogram of standard solution is presented in Fig. 1.

Table 1. Concentration of aldehydes and acetone in standard mixture

Compound	Synonyms	Acronime	Concentration, $\mu\text{g mL}^{-1}$
metanal	formaldehyde	FA	105
etanal	acetaldehyde	AA	76.4
propanon	acetone	AC	63.2
2-propenal	acrolein	ACC	61.5
propanal	propionaldehyde	AP	61.5
2-butenal	aldehyde crotonique	2-AB	53.6
n-butanal	butyl aldehyde	AB	52.5
benzaldehyde	benzaldehyde	BE	40.5
izopentanal	izovaleric aldehyde	IPE	46.4
pentanal	valeric aldehyde	PE	46.4
o-methylbenzaldehyde	o-methylbenzaldehyde	o-MB	37.5
m-methylbenzaldehyde	m-methylbenzaldehyde	m-MB	37.5
p-metylobenzaldehyde	p-metylobenzaldehyde	p-MB	37.5
heksanal	caproic aldehyde	ACA	42.0
2.5-dimethylbenzaldehyde	2.5-dimetylbenzaldehyde	DMB	35.0

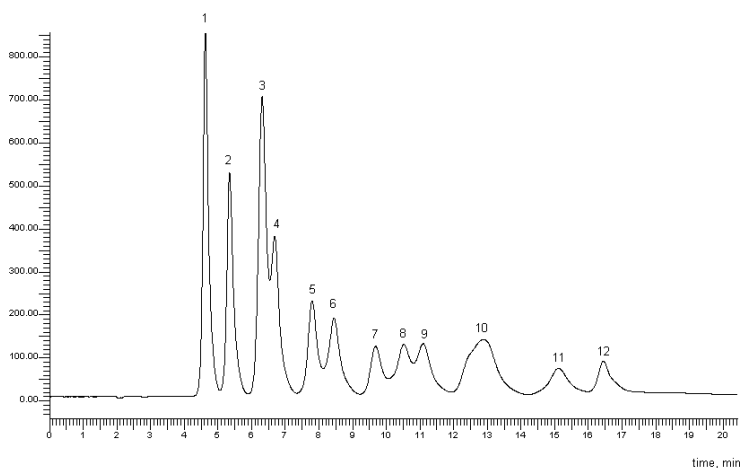


Fig. 1. Chromatogram of standard solution 1; FA ($105 \mu\text{g mL}^{-1}$). 2; AA ($76.4 \mu\text{g mL}^{-1}$). 3; ACC ($61.5 \mu\text{g mL}^{-1}$). 4; AC ($63.2 \mu\text{g mL}^{-1}$). 5; AP ($61.5 \mu\text{g mL}^{-1}$). 6; 2-AB ($53.6 \mu\text{g mL}^{-1}$). 7; AB ($52.5 \mu\text{g mL}^{-1}$). 8; BE ($40.5 \mu\text{g mL}^{-1}$). 9; IPE + PE ($46.4 \mu\text{g mL}^{-1} + 46.4 \mu\text{g mL}^{-1}$). 10; o-MB + m-MB+ p-MB ($37.5 \mu\text{g mL}^{-1} + 37.5 \mu\text{g mL}^{-1} + 37.5 \mu\text{g mL}^{-1}$). 11; ACA ($42.0 \mu\text{g mL}^{-1}$). 12; DMB ($35.0 \mu\text{g mL}^{-1}$).
Conditions: Spheri-10 RP-18 column (10 μm , $250 \times 4.6 \text{ mm}$), mobile phase: 60:40 acetonitrile-water

The limits of detection (LOD) were determined by progressively decreasing the concentration of the aldehydes spiked in the nanopure water until distinct responses were still clearly observed at a signal to noise ratio of 3. Limits of quantification (LOQ) are three times of LOD. LOD and LOQ for the standard solution are shown in Table 2. Calibration curve was prepared using seven concentration levels (0.0, 0.30, 0.50, 0.70, 0.90, 1.25, 1.88 $\mu\text{g mL}^{-1}$) and least squares linear regression was used to analyze the linearity.

Table 2. Limit of detection and determination of aldehydes and ketones

Compound	LOD, $\mu\text{g mL}^{-1}$	LOQ, $\mu\text{g mL}^{-1}$
formaldehyde	0.023	0.070
acetaldehyde	0.043	0.130
acrolein	0.007	0.020
acetone	0.017	0.050
Propionaldehyde	0.036	0.110
Aldehyde crotonique	0.007	0.020
N-Butyraldehyde	0.007	0.020
benzaldehyde	0.072	0.215
caproic aldehyde	0.079	0.240
2.5-dimethylbenzaldehyde	0.077	0.235

Pretreatment methods for wet deposition

In order to select the best separation method of aldehydes and ketones from wet deposition samples, studies were performed, where (i) extraction by SPE was preceded by derivatisation of the analytes – method A, and (ii) the simultaneous enrichment followed by SPE and derivatization of analytes – method B. Due to the physicochemical properties of aldehydes and ketones, mainly because of their volatility and ease of oxidation, studies to determine the optimal method for enrichment of aldehydes were carried out using working solution containing three compounds present in a standard: a formaldehyde, benzaldehyde and acetone in concentrations 1.50 $\mu\text{g L}^{-1}$ for formaldehyde, 1.26 $\mu\text{g L}^{-1}$ for acetone and 1.68 $\mu\text{g L}^{-1}$ for benzaldehyde. Derivatization for those two methods was performed using 2,4-dinitrophenylhydrazine solution obtained by dissolving 13.5 mg DNPH in 10 mL of 12 M hydrochloric acid, water (for HPLC) and acetonitrile in the ratio 2:5:1. For both methods A and B blank values and the relative standard deviations (RSD) were determined.

Method A – Derivatization in solution followed by solid phase extraction

The blank was prepared by adding 1 mL of prepared 2,4-dinitrophenylhydrazine solution to 250 mL of distilled water. In parallel, five working solutions were prepared and 1 mL of 2,4-dinitrophenylhydrazine solution was added. Then the pH of the samples was adjusted to pH 2 by using HCl and left for 12 h at room temperature. After the time required for derivatization, the samples were extracted with solid

phase on columns packed with C18 (500 mg) previously conditioned with 5 mL of acetonitrile and 5 mL of water. The sample flow rate through the column was 3 mL min⁻¹. The sorbed analytes were eluted from the bed with 1 mL of acetonitrile. Then the concentrated samples were analyzed by HPLC/DAD method. The study was repeated five times. Table 3 presents the obtained results. At the same time, in order to determine the blank values, the analysis of distilled water without addition of analytes was made in the same way.

Method B – Simultaneous enrichment followed by SPE and derivatization

The bed of a C18 column (500 mg) was conditioned with 5 mL of acetonitrile and 5 mL of water and then impregnated with 10 mL solution of 2,4-dinitrophenylhydrazine prepared according the procedure described above. After the step of impregnation, the column bed was dried by nitrogen stream. On such prepared bed, working mixture was added. The derivatized analytes were eluted with 1 mL of acetonitrile. The resulting eluate was analyzed by liquid chromatography. The procedure was repeated five times. The results of the analysis are shown in Table 3.

Table 3. Recovery of acetone and benzaldehyde in methods A and B

Parameter	Method A		Method B	
	Concentration of acetone, µg mL ⁻¹	Concentration of benzaldehyde, µg mL ⁻¹	Concentration of acetone, µg mL ⁻¹	Concentration of benzaldehyde, µg mL ⁻¹
Blank	0,47	no	0,76	0,07
Spiked of analyte	1,26	1,68	1,26	1,68
Recovery, %	92,8	97,0	98,4	99,4
RSD, %	18,6	10,4	5,6	4,5

no – not determined

Recovery determination

For both methods, based on the sample analysis after derivatization, the recovery of analytes was determined. The derivatization was carried out five times in accordance with method A and B. The results were related to the concentration of analytes in working solution. The results are shown in Table 3.

Environmental sampling

The samples were collected in dark glass vessels with a surface area of 0.22 m². The samples were preserved with HgCl₂ during sample collection and storage before analysis. Sampling points were located in agricultural areas and near the crossing of expressways in the heart of Silesian agglomeration – Poland (traffic source). Samples were taken during atmospheric precipitation. Table 4 shows the characteristics of the samples together with meteorological conditions such as rainfall intensity and ozone concentration in ambient air.

Table 4. Characteristic of sampling points

Number of sample	Date of sampling	Sampling place	Rainfall mm	Ozone concentration in air, $\mu\text{g m}^{-3}$
1	12.05.2010		8.6	50
2	17.05.2010		60.1	68
3	2.06.2010		17.8	42
4	13.06.2010	Agricultural area	2.6	68
5	14.06.2010		18.7	48
6	19.06.2010		3	60
7	6.07.2010		3.2	54
8	18.07.2010		13.6	72
9	13.05.2010		3.2	41
10	17.05.2010		39.2	72
11	22.05.2010	Source Communication	2.6	64
12	24.05.2010		4.0	56
13	15.06.2010		0.2	53
14	06.07.2010		1.2	47

RESULTS AND DISCUSSION

The method was characterized by a limit of quantification from $0.02 \mu\text{g mL}^{-1}$ to $0.24 \mu\text{g mL}^{-1}$ depending on the compound (Table 2). The data obtained from this work were compared with LODs of the common methods [3, 4]. In all cases, the correlation coefficients were greater than 0.999 which are acceptable for trace analysis. Aldehydes have no optical detectability, so their derivatization is a very important step from an analytical point of view. The derivatization procedures were optimised by recovery determination of two selected analytes: acetone and benzaldehyde. The recoveries in method A were 92.8% and 98.0% for acetone and benzaldehyde, respectively. The values for the blank sample were respectively $1.88 \mu\text{g L}^{-1}$ for acetone and below the LOQ for benzaldehyde. Method A was characterized by a RSD equal to 18.6% in the case of acetone and 10.4% for benzaldehyde. In method B, acetone and benzaldehyde recovery was 98.4% and 99.4% respectively, while the RSD was 5.6% for acetone and 4.5% for benzaldehyde (Table 3). Both methods were characterized by good recovery, however, due to the precision of the method expressed as RSD (Table 3), for testing of environmental samples the method B was used, in which the derivatization was carried out on C18 column.

Environmental samples

The analysis of wet deposition samples collected in the spring and summer showed that the total content of aldehydes ranged from $6.21 \mu\text{g L}^{-1}$ to $57.27 \mu\text{g L}^{-1}$ depending on the location of the sampling point (Tables 5, 6).

Table 5. The content of aldehydes and ketones in the wet deposition at the point located in agriculture areas, $\mu\text{g L}^{-3}$

Date of sampling	Formaldehyde	Acetaldehyde	Acrolein	Propionaldehyde	Aldehyde crotonique	Butyl aldehyde	Benzaldehyde	Total
12.05.2010	2.91	1.81	1.48	no	no	no	no	6.21
17.05.2010	2.95	2.38	1.64	no	no	no	no	6.97
02.06.2010	5.38	4.33	2.58	3.44	no	1.32	no	17.05
13.06.2010	14.30	4.99	6.86	3.62	1.32	no	no	31.09
14.06.2010	7.89	3.88	2.46	1.66	0.93	no	no	16.82
18.06.2010	9.70	4.73	2.59	9.28	2.89	no	no	29.19
06.07.2010	13.65	5.16	3.42	4.51	2.59	no	6.35	35.68
16.07.2010	24.47	10.51	6.74	9.03	3.33	no	3.20	57.27

no – not determined

Table 6. The content of aldehydes and ketones in wet deposition at a point located near the source of the communication, $\mu\text{g L}^{-3}$

Date of sampling	Formaldehyde	Acetaldehyde	Acrolein	Total
13.05.2010	4.52	3.25	14.49	22.53
17.05.2010	4.66	4.15	11.9	20.71
22.05.2010	4.88	4.45	15.19	24.52
24.05.2010	4.92	2.97	13.70	21.59
15.06.2010	4.82	2.47	11.70	18.99
06.07.2010	4.75	3.67	14.98	23.40

In all cases, the dominant aldehyde was formaldehyde, the concentration of this compound changing from $2.47 \mu\text{g L}^{-1}$ to $14.3 \mu\text{g L}^{-1}$. The proportion of formaldehyde in the total identified compounds varies depending on the point of sampling. In agricultural areas it was from 31% to 47% (Fig. 2) of the determined compounds, while in the case of a point located near the source of the communication the contribution of formaldehyde ranged from 20% to 25%. A diversified profile of aldehydes was also observed, since in the case of wet deposition samples collected from agricultural areas in addition to formaldehyde, presence of acetaldehyde, acrolein, aldehydes propionic, crotonic, butyl and benzaldehyde was noticed. In the samples from sources of the traffic only three carbonyl compounds occurred such as formaldehyde, acetaldehyde and acrolein. The acrolein was the dominant compound in traffic samples (Table 6). The concentration of acrolein in the wet deposition ranged from $11.7 \mu\text{g L}^{-1}$ to $15.19 \mu\text{g L}^{-1}$, which constituted from 62% to 64% of the determined compounds (Fig. 3). In the case of agricultural areas concentration of this compound was from $1.48 \mu\text{g L}^{-1}$ to $6.86 \mu\text{g L}^{-1}$ and it was from 9% to 23% of the determined analytes. The diverse profile of aldehydes, depending on the characteristics of the sampling point is expressed also by the weight ratios of individual compounds. In all described samples the ratio of formaldehyde to acetaldehyde ranged from 1.1 to 2.6, whereas in the case of acrolein, formaldehyde concentration ratio to acrolein in samples taken from agricultural areas ranged from 2 to 4, while in samples collected near sources of the traffic remained at 0.3–0.4. This relationship indicates that in the case of traffic sources the acrolein is the main pollutant present in the wet deposition.

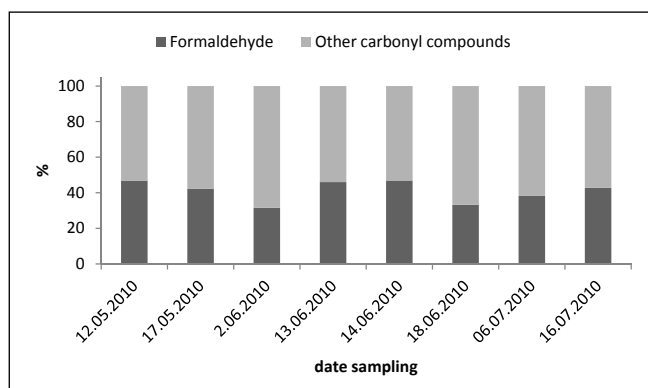


Fig. 2. Distribution of formaldehyde and other carbonyl compounds for point located in agriculture areas

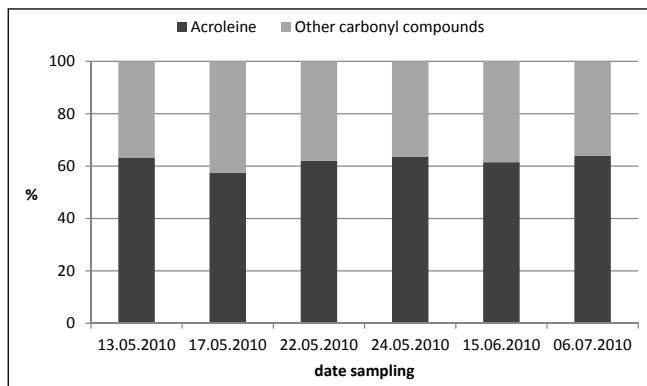


Fig. 3. Distribution of acroleine and other carbonyl compounds for point located near the traffic source

CONCLUSION

The study showed that both methods of determination of trace aldehydes in liquid samples are characterized by good recovery (above 90%). However, due to the higher recovery of carbonyl compounds and improved accuracy of the method B, this method was used for analyzing environmental samples. The analysis of wet deposition samples showed, that (i) in samples collected in agricultural areas, the formaldehyde and acetaldehyde were predominant aldehydes, (ii) while in the samples collected near a traffic source the dominant carbonyl compound was acrolein.

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OZNACZANIE ALDEHYDÓW W DEPOZYCJI MOKREJ

W pracy przedstawiono dwie procedury przygotowania próbek mokrej depozycji do oznaczeń aldehydów. W obydwóch przypadkach zastosowano derywatyzację 2,4-dinitrofenylohydrazyną oraz ekstrakcję do fazy stałej. W metodzie A derywatyzacja poprzedzała ekstrakcję, w metodzie B ekstrakcję prowadzono z równoczesną derywatyzacją. Na podstawie analiz wodnych roztworów wybranych związków karbonylowych oceniono precyzję obydwóch metod. Ze względu na odzysk oraz wartość względnego odchylenia do analiz próbek środowiskowych pobranych z obszarów silnie uprzemysłowionych i rolniczych wybrano metodę B.

Analiza próbek środowiskowych wykazała znaczne zróżnicowanie stężeń aldehydów w mokrej depozycji w zależności od lokalizacji punktu pobierania próbek. W przypadku próbek pobranych z obszarów rolniczych dominującymi aldehydami były formaldehyd i acetaldehyd. Formaldehyd stanowił od 31% do 47% oznaczonych związków. Podczas gdy w próbkach pobranych w pobliżu źródeł komunikacyjnych w depozycji stwierdzono udział akroleiny w oznaczonych aldehydach na poziomie od 62% do 64% oznaczonych związków.