

## Specific Features of the Determination of Carbonyl Compounds in Atmospheric Air

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**Abstract**—It has been shown that the error of the determination of formaldehyde in atmospheric air depends both on the method of measurement of the analytical signal and on the conditions of air sampling. In most cases, the use of HPLC leads to underestimated results, while the application of spectrophotometry leads to overestimated results. A method has been developed for the selective determination of formaldehyde in atmospheric air using HPLC with a fluorescence detector, which can be used as a reference method.

**Keywords:** formaldehyde, aldehydes, 2,4-dinitrophenylhydrazine, acetylacetone, HPLC, spectrophotometry, atmospheric air

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Carbonyl compounds belong to priority pollutants of atmospheric air. The most toxic carbonyl compound is formaldehyde, which possesses carcinogenic and immunosuppressing properties [1–4]. Formaldehyde is included in the list of substances determining the high level of ambient air pollution in cities; therefore, generation of reliable data on its concentration in air is an important task.

Air monitoring is among the most complicated analytical procedures. Each of the stages of analysis, sampling and preconcentration of air samples, their storage, and method of signal measurement, introduces a certain error into the final result. For example, the incomplete trapping of components during sampling and the loss of analytes due to their breakthrough, adsorption, etc. can occur. In formaldehyde analysis, one should take into account its high reactivity, which depends on the temperature of environment, solar radiation, etc. Moreover, oxidants (ozone, nitrogen and sulfur oxides, etc.) and impurities of other organic compounds also affect the results of analysis [2, 5–10].

Atmospheric air is an extremely fast-moving component of the environment and this feature complicates the possibilities of the simulation of experimental conditions the close to the natural. Different methods were described for the elimination of some factors affecting the determination of formaldehyde in air; however, the reasons for a significant discrepancy between the results obtained by different methods have been revealed insufficiently.

In the present work, we studied the effect of conditions of air sampling on the results of analysis and developed a method for the determination of formaldehyde by HPLC taking into account the artifacts revealed.

### EXPERIMENTAL

**Equipment.** A LC 20-AD liquid chromatograph (Shimadzu, Japan) consisted of a gradient pump, a flow eluent degasser, a thermostat, a Rheodyne injector, a diode-array detector (DAD), and a Supelco C<sub>18</sub> analytical column (250 × 2.1 mm × 5 μm). The separation of components was performed in the gradient elution mode using a mixture of acetonitrile with water and flow rate of 0.3 mL/min. Column temperature was 35°C. Sample injection volume was 5 μL. The components were identified by retention times and absorption spectra. The data obtained were processed using the LC Solution software.

A Waters liquid chromatograph (United States) was equipped with a gradient pump, an U6K universal injector, a Waters 474 fluorescence detector, and a Vydac 201 TP 54-C<sub>18</sub> analytical column (250 × 4.6 mm × 5 μm). The data obtained were processed using the Millenium<sup>32</sup> software (REV.3.2, Waters, United States).

A KFK-3 photocolormeter (Russia) and 1-cm cells were used.

**Reagents and materials.** Acetonitrile (Kriokhrom, St. Petersburg, Russia) of grade 0 was used; twice-distilled water was purified on a Milli-Q purifying system

**Table 1.** Determination of formaldehyde (mg/m<sup>3</sup>) in atmospheric air by HPLC and photometry ( $n = 5$ ,  $P = 0.95$ )

Sampling point	HPLC	Photometry
Parkland (Ufa)	0.0026 ± 0.0007	0.017 ± 0.003
Rossiyskaya ul. (Ufa)	0.0120 ± 0.0030	0.028 ± 0.006
Meadow at the north-west of village Mikhailovka	0.0029 ± 0.0007	0.022 ± 0.004
Wetland	0.0054 ± 0.0014	0.024 ± 0.005

(Millipore, United States). Experiments were performed using State Standard Samples (SSSs) of formaldehyde (metanal), SSS of acetone, as well as standards of acetaldehyde (ethanal), propionaldehyde (propanal), crotonaldehyde (*trans*- $\beta$ -metacrylic aldehyde), pelargonic aldehyde (nonanal), capric aldehyde (decanal), benzaldehyde (all Sigma-Aldrich), butyraldehyde (butanal), valeraldehyde (pentanal), isovaleraldehyde (3-methylbutanal), caproaldehyde (hexanal), heptanaldehyde (heptanal), octyl aldehyde (octanal), *m,p*-toluyl aldehyde (all from Aldrich), *o*-toluylaldehyde (Fluka), 2,4-dinitrophenylhydrazine (**2,4-DNPH**) of reagent grade, acetylacetone of analytical grade, ammonium acetate of analytical grade, glacial acetic acid of cp grade, orthophosphoric acid of cp grade, and hydrochloric acid of cp grade (Russia).

**Hydrazones of carbonyl compounds were prepared** according to [10]. An equimolar amount of a carbonyl compound was added to 300 mL of a 0.2% 2,4-DNPH solution. The precipitate of 2,4-dinitrophenylhydrazone of the corresponding carbonyl compound was separated by filtration, washed with 2 M HCl and then with water, and dried in air to a constant weight.

**Quantitative determination of carbonyl compounds by HPLC** was performed using absolute calibration. The correlation coefficients for the calibration curves were 0.994–0.999.

**Determination of formaldehyde by photometry** was performed according to [11].

**Air sampling.** Air samples for analysis by HPLC with DAD were collected in chemisorption tubes with 2,4-DNPH, which were prepared beforehand. With this purpose, Silochrom C-120 was placed into sorption tubes and washed with acetonitrile; then a 0.01% 2,4-DNPH solution in acetonitrile containing 1% of orthophosphoric acid was passed through the adsorbent layer, and the adsorbent was dried in an air flow. Air sample was aspirated at a flow rate of 0.3 L/min for 20 min.

Air samples for photometric analysis were collected according to the method [11].

The studies were performed using model mixtures and also in field conditions.

## RESULTS AND DISCUSSION

It is known that the determination of formaldehyde as 2,4-dinitrophenylhydrazone by HPLC gives results 15–20% lower compared to the results of photometric analysis [12]. Experiments with model mixtures, as well as analysis of air in the laboratory and other facilities using HPLC and photometry performed in this study, resulted in the generation of irreproducible results. However, a comparison of the data obtained by these methods under field conditions (Table 1) shows that the discrepancy between the results of determination formaldehyde 2,4-dinitrophenylhydrazone of by HPLC and the results of the photometric determination of 3,5-diacetyl-1,4-dihydrolutidine is much larger. The most probable reasons for this discrepancy can be provided by errors arising in air sampling under natural conditions. Atmospheric air is characterized by the occurrence of photochemical, physicochemical, and other processes, and these processes cannot be simulated in a laboratory experiment. Ultimately, the occurrence of the indicated processes, meteorological conditions, composition of pollutants in the atmosphere and their concentrations, as well as the proper selection of absorbers, sorbents, air flow rate, etc., affect the efficiency of trapping analytes and the results of analysis.

**Selection of the conditions of analysis. Air sampling.** To select the working conditions of sampling with an aspirator, equal volumes of air were passed through chemisorption tubes at different flow rates. The eluates were analyzed on a liquid chromatograph with a DAD. The effectiveness of trapping formaldehyde was evaluated by peak areas in chromatograms. It was found that, in sampling at a flow rate of 0.2–0.4 L/min, the maximum efficiency of formaldehyde preconcentration was achieved. Solvent volume needed for the desorption of analytes, possibility of breakthrough of the determined components during sampling, and the time of storage of the collected samples were also studied. Based on the results of experiments performed, the following conditions of the collection of air samples were selected: aspiration flow rate 0.3 L/min, desorption of analytes with 1 mL of acetonitrile, samples storage in a refrigerator in a hermetically sealed container up to 1 month.

**Effect of nitrogen dioxide.** Chemisorption of formaldehyde with 2,4-DNPH is the most widespread method of sampling in determination by HPLC. However, the reagent used for the preparation of the derivative can be spent not only for interaction with the analyte, but also for the reaction with nitrogen dioxide and other pollutants present in atmospheric air. The result will be underestimated in the lack of the reagent and overestimated if by-products, which have characteristics similar with those of the target component chromatographic, formed.

Nitrogen dioxide reacts with 2,4-DNPH with the formation of 2,4-dinitrophenyl azide (the main prod-

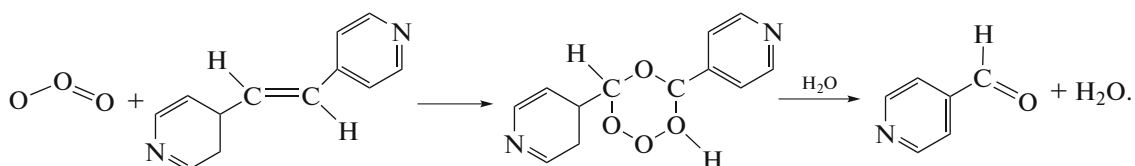
**Table 2.** Determination of aldehydes (mg/m<sup>3</sup>) in samples of atmospheric air in the city of Ufa (I) with and (II) without cartridges with BPE for trapping ozone ( $n = 5$ ,  $P = 0.95$ )

Compound	I	II
Formaldehyde	0.014 ± 0.004	0.008 ± 0.002
Acetaldehyde	0.004 ± 0.004	0.0010 ± 0.0003
Propanal	0.12 ± 0.03	0.005 ± 0.001
Butanal	0.0030 ± 0.0008	0.0020 ± 0.0005
Isovaleric aldehyde	0.004 ± 0.001	0.004 ± 0.001
Pentanal	0.007 ± 0.002	0.004 ± 0.001
<i>o</i> -Toluic aldehyde	0.005 ± 0.001	0.001 ± 0.0003
<i>m,p</i> -Toluic aldehyde	0.005 ± 0.001	0.0010 ± 0.0003
Hexanal	0.0030 ± 0.0008	0.001 ± 0.0003
Heptanal	0.006 ± 0.002	0.0020 ± 0.0005
Octanal	0.011 ± 0.003	0.005 ± 0.001
Nonanal	0.005 ± 0.001	0.0020 ± 0.0005
Decanal	0.010 ± 0.003	0.0020 ± 0.0005

uct) and 2,4-dinitrochlorobenzene (by-product) [5]. The effect of nitrogen dioxide was studied by passing a control gas mixture with different NO<sub>2</sub> concentrations through sorption tubes to which the known amounts of formaldehyde and other carbonyl compounds were preliminarily added. It was found that, in an excess of 2,4-DNPH, the presence of nitrogen dioxide in air did not affect the analytical signal of formaldehyde hydrazone. The amount of 2,4-DNPH was controlled by the peak in the chromatogram. If high concentrations of nitrogen dioxide, formaldehyde, and other compounds are expected in an air sample (for example, in

gaseous waste), one should use two sequentially connected chemisorption tubes for sample preparation.

*Effect of ozone.* Ozone present in air reacts with 2,4-DNPH and also with aldehyde hydrazones [2, 9]. Various methods of elimination of the interfering effect of ozone were proposed [2, 8, 10]. We found that *trans*-1,2-bis(4-pyridyl)ethylene (**BPE**) is the most efficient reagent for trapping ozone. When ozone reacts with BPE, ozonide (intermediate product) formed and then 4-pyridincarboxaldehyde [8]:

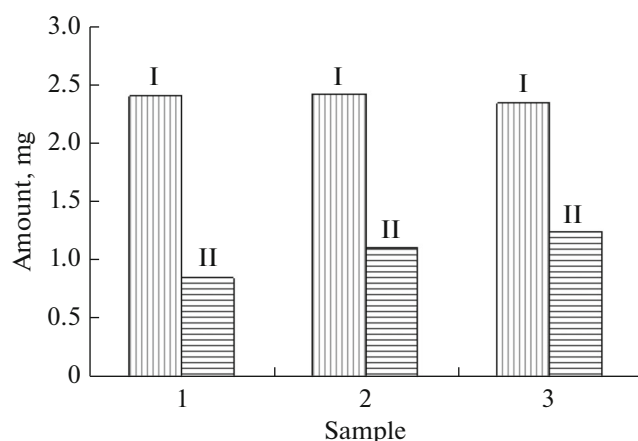


To trap ozone during air sampling, cartridges with the sorbent with a preliminarily applied BPE solution in acetonitrile were installed in front of chemisorption tubes with 2,4-DNPH. The results obtained are presented in Table 2. It should be noted that the use of BPE offers a possibility of the simultaneous determination of both carbonyl compounds and ozone as 4-pyridincarboxaldehyde in one air sample.

*Effect of relative air humidity.* Formaldehyde in aqueous media is present in the hydrated form. In particular, formaldehyde in aqueous solutions forms methylene glycol or hydrates of polymers (dimer, trimer, up to octamer). We can suppose that hydrates also form in humid air media, which finally results in a decrease of the reactivity of formaldehyde. It was shown experimentally that elevated air humidity

(higher than 80%) leads to an approximately two-fold underestimation of the results of analysis. The use of desiccants, such as calcium chloride, sodium sulfate, silica, and others, results in the underestimation of the results of analysis. The introduction of correction factors taking into account the change in the concentration of formaldehyde depending on relative air humidity can be a solution of this problem.

*Other aldehyde pollutants present in the analyzed air* cause underestimation of the results of formaldehyde determination (Fig. 1). Experiments were performed using artificial mixtures of formaldehyde and other aldehydes in the ratio 1 : 1, 2 : 1 and 4 : 1. It was found that the lower the concentration of other aldehydes in the sample, the higher the reliability of formaldehyde determination. Presumably, in the presence of ele-



**Fig. 1.** Effect of aldehyde pollutants in air on the results of formaldehyde determination: I, air sample contains formaldehyde, II, air sample contains formaldehyde in a mixture with other aldehydes in the ratio 1 : 1, 2 : 1 and 4 : 1 (samples 1–3 respectively).

vated concentrations of other aldehydes in air, the results of analysis are distorted because of the predominant consumption of the reagent for interaction with these compounds rather than with formaldehyde. It should be noted that formaldehyde is the most abundant aldehyde in atmospheric air. If there are sources of elevated pollution of air by other carbonyl compounds, this fact must be taken into account in sampling. For example, trapping of the determined components in two sequentially connected chemisorption cartridges allows the analyst to attain satisfactory results of analysis.

**Method of formaldehyde determination by HPLC with a fluorescence detector.** In the determination of formaldehyde by HPLC (as hydrazone) and photometry (as 3,5-diacetyl-1,4-dihydrolutidine), it is trapped from air by various methods; therefore, the contribution of sampling to the total error of formaldehyde determination can hardly be distinguished. To reveal possible artefacts at the stage of sampling, we

**Table 3.** Determination of formaldehyde ( $\text{mg}/\text{m}^3$ ) in samples of atmospheric air of the city of Ufa using different methods ( $n = 3$ ,  $P = 0.95$ )

Sample	Photometry*	HPLC	
		fluorescence detector*	DAD**
1	$0.020 \pm 0.005$	$0.017 \pm 0.004$	$0.013 \pm 0.003$
2	$0.033 \pm 0.006$	$0.017 \pm 0.004$	$0.011 \pm 0.003$
3	$0.036 \pm 0.009$	$0.016 \pm 0.004$	$0.014 \pm 0.004$
4	$0.04 \pm 0.01$	$0.015 \pm 0.004$	$0.012 \pm 0.003$

\* Sampling in traps with acetylacetone. \*\* Sampling in a sorption tube with 2,4-DNPH and BPE.

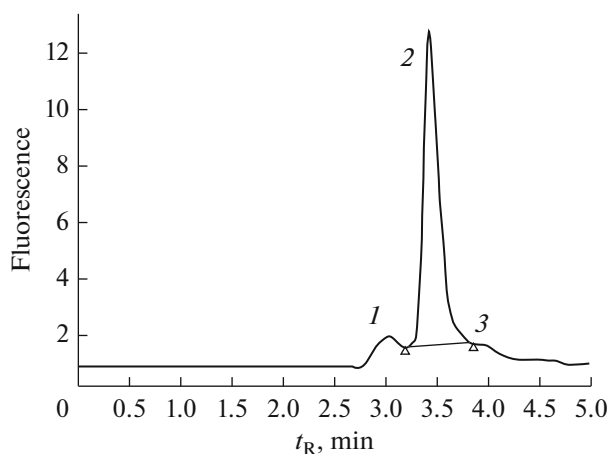
developed a method including the derivatization of formaldehyde with acetylacetone followed by its determination by reversed-phase HPLC with fluorescence detection. Separation was performed in the isocratic mode using an acetonitrile–water (50 : 50, v/v) mobile phase at a flow rate of 1 mL/min. Sample injection volume was 20  $\mu\text{L}$ , temperature of column thermostat was 35°C. Analysis was performed at the excitation wavelength 410 nm and emission wavelength 512 nm.

A trapping solution for the extraction of formaldehyde from air samples was prepared as follows: 150 g of  $\text{CH}_3\text{COONH}_4$  was dissolved in 800 mL of water, then 2 mL of acetylacetone and 3 mL of glacial acetic acid were added, the mixture was thoroughly stirred and diluted to the mark with water. The prepared solution (6 mL) was added to traps. An air sample was aspirated through two sequentially connected traps at a flow rate of 1 L/min for 30 min; 100  $\mu\text{L}$  of the solution was taken with a microsyringe and analyzed on a liquid chromatograph with a fluorescence detector; the remained solution was analyzed by photometry according to method [11].

#### Study of atmospheric air samples of the city of Ufa.

The air analysis of samples was performed using three techniques: photometric, HPLC with a DAD, and HPLC with a fluorescence detector according to the developed method. Air samples were trapped in traps filled with an acetylacetone solution and in chemisorption tubes filled with Silochrom C-120 impregnated with 2,4-DNPH (cartridges with BPE for trapping ozone were installed before the sorption tube). This experiment ensures the evaluation of the difference between the results of analysis of an air sample collected simultaneously depending on the sampling conditions and the method of measurement of the analytical signal. The results obtained are presented in Table 3. It can be seen that the results of analysis of the same trapping solutions containing acetylacetone obtained by photometry and HPLC with a fluorescence detector were different. Since sampling conditions in this case were identical, the error of formaldehyde determination is associated with the method of signal measurement. HPLC with a fluorescence detector is a selective method of analysis; consequently, the results obtained by photometry were overestimated, presumably, because of the presence of pollutants in the studied air absorbing in the same wavelength range as the analytical form of formaldehyde. The results of analysis of the air samples by HPLC with a DAD and a fluorescence detector were comparable (Table 3).

Figure 2 presents a chromatogram of an air sample recorded on a liquid chromatograph with a fluorescence detector. It can be seen that the retention times of impurities present in the sample insignificantly differ from the retention time of the analytical form of formaldehyde 3,5-diacetyl-1,4-dihydrolutidine.



**Fig. 2.** Chromatogram of an air sample on a Vydac 201 TP54 C<sub>18</sub> column (250 × 4.6 mm, 5 μm) in elution with an acetonitrile–water (50 : 50, v/v) mixture with a fluorescence detector (410/512 nm): 1, 3, impurities; 2, 3,5-diacetyl-1,4-dihydrolutidine.

Thus, the error of formaldehyde determination by HPLC with DAD significantly depends on sampling conditions, while in photometric determination it depends on the method of measurement of the analytical signal. With the thorough elimination of interfering factors at the sampling stage, HPLC with DAD is the preferable method of air analysis. The possibility of the simultaneous determination of other carbonyl compounds in addition to formaldehyde, as well as of ozone, if necessary, can be considered as an advantage of HPLC. The use of a fluorimeter instead of a photocolormeter ensures the reduction of the error of analysis. The developed selective method of analysis of air samples using HPLC with fluorescence detector can be used as a reference method.

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