Spectroscopic Analysis of Organic Matters Derived from Urban Atmospheric Aerosols

A.A. Uspenski and A.V. Stepakov*

Voeikov Main Geophysical Observatory, ul. Karbysheva 7, St. Petersburg 194021, Russian Federation

*Corresponding author: E-mail: alstep@yandex.ru

The composition of organic matter derived from $PM_{2.5}$ fraction of urban aerosols collected in Saint-Petersburg during the annual cycle was investigated by ^1H NMR, ^{13}C NMR and IR spectroscopies. It was found that the composition of organic fraction varies slightly with the seasons. The main organic components of aerosol extracts are aliphatic oxygen-containing compounds (such as derivatives of carboxylic acids and esters), whose content is maximum in winter samples. Aromatic compounds are present in aerosol extracts in negligible quantities. The results showed a significant contribution of the process of combustion of automotive fuel in the formation of low molecular weight organic compounds that are present in the composition of urban aerosol.

Keywords: NMR spectroscopy, IR spectroscopy, $PM_{2.5}$ fraction, Atmospheric aerosols, Organic compounds.

INTRODUCTION

Nuclear magnetic resonance is one of the absorption methods, along with infrared spectrometry. Substance under certain conditions can absorb electromagnetic radiation in the radio frequency range. Narrow absorption peaks are associated with the presence of certain nuclei in the molecules. The eigen value of the resulting dipole is expressed in terms of the nuclear magnetic moment. Each proton and neutron has an intrinsic spin, and their interaction leads to a spin quantum number. If the sum of the numbers of protons in the nucleus is even, then the spin quantum number is zero or an integer. In case if the sum is odd, then the quantum spin number takes half-integral values. For a proton, two orientations are possible in an external uniform magnetic field. The first state is characterized by stability and lower energy. The position of the energy levels depends on the magnitude of the nuclear magnetic moment and the strength of the external magnetic field. When a quantum of energy is absorbed, the proton can pass from the lower level to the upper (anti-parallel orientation). Such a change is accompanied by the absorption of electromagnetic energy [1]. Apart from the mechanism of the transition of nuclei to a higher energy state upon energy absorption, there is an inverse process. In the absence of an inverse process, the nuclei would pass into an excited state and the absorption of energy in this case would

cease. A nucleus in an excited state can transmit an excess of energy and return to a lower state. Energy can be distributed between the nuclei, or transmitted to the molecular lattice. Another absorption method is infra-red spectrometry [1]. IR radiation with a frequency of less than 100 cm⁻¹ is absorbed by the molecule and converted by an organic molecule into rotational energy. Absorption is quantized, the rotational spectrum of molecules consists of discrete lines. IR radiation in the interval 10000-100 cm⁻¹ under absorption is converted by an organic molecule into vibrational energy. The frequency at which the absorption band is observed depends on the relative masses of nuclei, the force constants of bonds, and the geometry of molecule. There are two types of molecular vibrations-stretching and bending [1]. Stretching oscillations are rhythmic movements along the axis of communication with the change in the interatomic distance (increase or decrease). Bending oscillations consist in changing the angle formed by the bonds [1].

Qualitative analysis of the composition of $PM_{2.5}$ fraction using these methods makes it possible to identify the components of atmospheric air sorbed on the particles. At the moment, particular attention is paid to the finely dispersed fraction of atmospheric aerosol. The impact of $PM_{2.5}$ can lead to an increase in morbidity and mortality, including the incidence of cancer, changes in the climate system, warming up the atmosphere and the ability of particles to act as the nuclei of condensation

nuclei, the possibility of reducing the cloud cover [2]. Special attention in this work is paid to the identification of carboxylic acid's functional groups. Derivatization was carried out under certain conditions for this purpose. The abundance of these functional groups can affect on cloud condensation nuclei (CCN) abilities of organic particles within the aerosol′s composition [3]. A derivatization provides to convert carboxylic acids into the corresponding methyl esters, which show a clearly-expressed band in the ^{1}H NMR spectrum [4]. Atmospheric aerosol particles are inherently complex mixture of inorganic and organic substances. Organic fraction is usually 20-90 % of the total submicron aerosol mass and is much less limited in chemical composition than inorganic fraction [5]. The mortality rate may increase approximately within the following limits: by 0.2-0.6 % per 10 µg/m^3 of PM_{10} in the cause of PM_{10}. The risk of cardiopulmonary mortality by 6-13 % per 10 µg/m^3 $PM_{2.5}$ is observed in the case of prolonged exposure to particles by inhalation [6-10]. There is sufficient evidence of the ability of the particles to corrode the alveolar walls, disrupting the functioning of the lungs [11]. There is a correlation between the presence $PM_{2.5}$ fraction in urban air and mortality, the formation of smog is also a consequence of prolonged presence of particles in the atmosphere [12,13]. The $PM_{2.5}$ particles can penetrate even into epithelial cells and alveolar macrophages after sedimentation in bronchioles and alveoli [14]. Deaths resulting from apoptosis, autophage or cell function disorders may occur as a result of oxidative stress [14]. Inflammatory reactions appear during the infiltration of inflammatory cells and the release of inflammatory mediators [14]. Alveolar collapse can be caused by the disorder of the net of cytokines and damage of lung tissue [14]. Chronic bronchitis, chronic obstructive pulmonary disease (COPD) and asthma can occur with the flow of a constant oxidative and inflammatory process, associated with the presence of particles inside [14]. Worsen bronchial mucociliary system, and as a side effect of reducing the bacterial clearance arises from the harmful effect of $PM_{2.5}$ [14]. In some works, the seasonal variability of aerosol concentration was studied. Average mass concentrations was observed in spring (2.2 ± 0.7 µg/m^3) and summer (1.9 ± 0.7 µg/m^3), in autumn (1.2 ± 0.3 µg/m^3) and winter (1.2 ± 0.5 µg/m^3). It can be attribute to the heavy traffic emission from Xinsheng Highway (Taiwan) during the process of photochemical nucleation (in dependence of intense solar radiation in a warm period) [15]. There is dataset of an inverse relation: the observed concentration of $PM_{2.5}$ in winter and autumn was higher than in spring and summer [16]. The $PM_{2.5}$ matters in lung tissue can affect the blood coagulation system or induce thrombosis which subsequently can lead to lesion of angiostenosis, such as myocardial infarction and cerebral infarction [17]. The immune capacity of macrophages is also worsening and can be weakened, which reduces counterstand to infection. DNA can be damaged by macrophages, while they attack $PM_{2.5}$ accumulates in the lung tissue, therefore $PM_{2.5}$ can cause cancer [17]. The predominant part of $PM_{2.5}$ is the carbonaceous component of combustion and secondary ammonium nitrate/sulfate in urban air [18]. Risk of ischemic stroke, cardiac ischemia and coronary artery disease can be caused by particulate matter prolonged exposure [19-21].

^{1}H NMR spectroscopy has already been used to characterize aerosols from biomass burning and as a method of identification of the source of water soluble organic compounds (WSOC) [22]. NMR spectroscopy was applied for further research of the functional group composition of biomass aerosol burning. Aliphatic carbonyls or carboxylic groups can be detected by ^{1}H NMR spectroscopy indirectly due to absence of detectable protons. Based on intensity of resonances between 1.9 and 3.0 ppm, chemical shift can be assigned to aliphatic groups adjacent to an unsaturated carbon atom, HC-C=O, HC-COOH or HC-C=C [22]. Methodology in some recent works for direct determination of carbonyls and carboxylic groups includes the coupling chemical derivatization to ^{1}H NMR spectroscopy [22]. Carboxylic acids convert to methyl esters through chemical reaction with diazomethane. Integration of band between 3 and 4 ppm in the ^{1}H NMR spectrum after substraction signals (underivatized samples) can provide such an opportunity. For carbonyls there is a similar process, when the samples were derivatized in methyl oxime through reaction with O-methyl-hydroxylamine [22]. In our previous work, mass spectrometric methods were used to carry out a qualitative analysis of atmospheric aerosol samples, which made it possible to identify many polyaromatic components [23]. This work is a logical continuation previous research.

EXPERIMENTAL

The ambient aerosols were collected on a monitoring station of Voeikov Main Geophysical Observatory, St. Petersburg, Russia, situated close to the street with a relatively strenuous traffic. For collecting the aerosol samples aspirator Derenda LS was used. The $PM_{2.5}$ aerosols samples were assembled on quartz filters GF 10 (Whatman™) at a flow rate of 38 L/min. Long-term sampling of aerosol (24 days) was preferable owing to the need to accumulate the required number of aerosol for further analysis (NMR and IR). After sampling, quartz filters with aerosol samples were delivered to our laboratory in sealed plastic bags. Prior to the analysis, samples were stored in the refrigerator at −25 ºC. Extraction of samples was carried out using a Soxhlet system with dichloromethane as solvent in argon atmosphere. After the extraction was completed, dichloromethane was evaporated and the residue was analyzed by ^{1}H, ^{13}C NMR and IR spectroscopy. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer and ^{13}C NMR spectra were recorded on 100 MHz instrument ($CDCl_3$). Chemical shifts (δ) in ppm are reported with the use of the residual chloroform (7.26 ppm for ^{1}H and 77.2 ppm for ^{13}C NMR). IR spectra were measured in KBr and wavelengths are reported in cm^{-1}. Diazomethane for derivatization of aerosol extract was prepared by hydrolysis of an ethereal solution of an *N*-nitroso-*N*-methylurea with aqueous base (40 % aq. KOH) [24].

Derivatization procedure: Diazomethane solution in diethyl ether was prepared from *N*-nitroso-*N*-methylurea (0.5 g). To an aliquot of aerosol extract (15 mg in 5 mL ethyl ether), 5 mL of ethereal CH_2N_2 solution were added and the resulting clear light-yellow solution was kept at room temperature for 1 h and evaporated under vacuum; the residue was dissolved in $CDCl_3$ and used for ^{1}H NMR analysis.

RESULTS AND DISCUSSION

In this work, the ^{1}H NMR spectra of extracts of urban aerosol samples collected at different times of the year were analyzed. As can be seen from Figs. 1-4, in all cases the spectra have signals in similar areas, which indicates the constancy of the organic components in the composition of urban aerosols. Aromatic protons appear in the spectral region between 7.0 and 8.0 ppm like a weak continuous band. The maximum is in the region of 7.2-7.4 ppm, which suggests that electron-acceptor substituents in the aromatic rings (carbonyl, carboxyl, *etc.*) are more common than the electron-donating substituents (hydroxyl, alkoxyl, alkyl, amino). Aldehyde protons were not observed at 9-11 ppm. A relatively intense continuous spectrum of aliphatic protons is observed between 0.7 and 4.2 ppm. Aliphatic protons are peculiarly common in the following areas: 0.5-1.0 ppm (methyl groups), 1.2-1.7 ppm (methylene groups of aliphatic chains), 2.1-2.5 ppm - weak broad signals of aliphatic protons on carbon atoms adjacent to carbonyl groups, or aromatic rings) and 3.5-4.2 ppm (alcohols and ethers). Intensive signals in the region of 3.5-4.2 ppm indicate a fairly high concentration of hydroxy and (or) ether derivatives. No signals in the spectral region between 2.7 and 3.4 ppm suggest that aliphatic amines (AlkNH$_2$) and alkylsulfonates (AlkSO-) and their presence can be considered in essentially low concentrations (only in one case, a weak signal in the region of 3.0 ppm is recorded, which can be attributed to aliphatic amines; Fig. 2).

The above data can be summarized by identifying the four most representative categories of functional groups in the ^{1}H NMR spectra of urban aerosol samples (Figs. 1-4): Ar-H: aromatic protons (7.0-8.0 ppm); H-C-O: protons on carbon atoms, uniquely associated with oxygen atoms (3.5-4.2 ppm); H-C-C=O (H-C-Ar): aliphatic protons on carbon atoms adjacent to carbonyl groups or aromatic rings (2.1-2.5 ppm); and H-C: aliphatic protons (0.5-1.7 ppm) [25-27].

Further, using the methylation reaction of carboxyl groups with diazomethane, one can determine the presence of aliphatic carboxylic acids in the aerosol extract. After chemical derivatization of the aerosol extract using diazomethane, a new signal appeared at its ^{1}H NMR spectrum at 3.68 ppm, which was absent in the spectrum of the untreated sample (Fig. 4). This signal, with a high probability, can be attributed to aliphatic carboxylic acid methyl ester. From the analysis of ^{1}H NMR spectra, it can be seen that the main organic components of aerosol extracts are aliphatic oxygen-containing compounds with a low content of aromatics. The obtained spectral data do not provide to make an inference about the presence of aldehydes, aliphatic nitro compounds and amines in aerosol extracts.

From ^{13}C NMR spectrum (Fig. 5), it can be seen that the aerosol extract contains a wide range of saturated aliphatic components, as indicated by signals in the range of 13-51 ppm. For example in ^{13}C NMR spectrum, the signals are observed at 19.1 ppm and in the region of 30 ppm, which can be attributed to the methylene and methine groups of the alkyl chains,
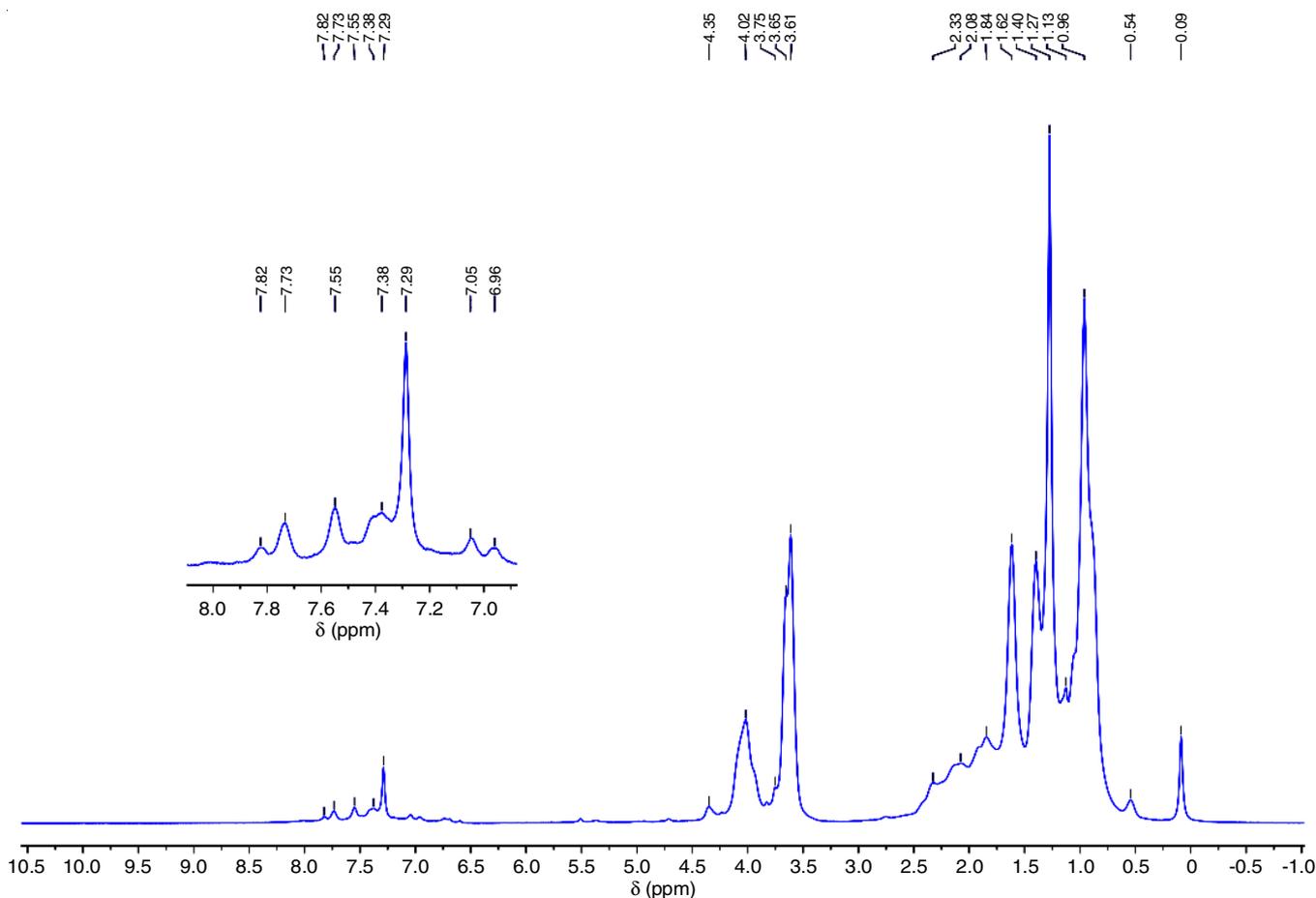
Fig. 1. ^{1}H NMR spectrum of the dichloromethane extract of urban aerosol sample collected in the winter season
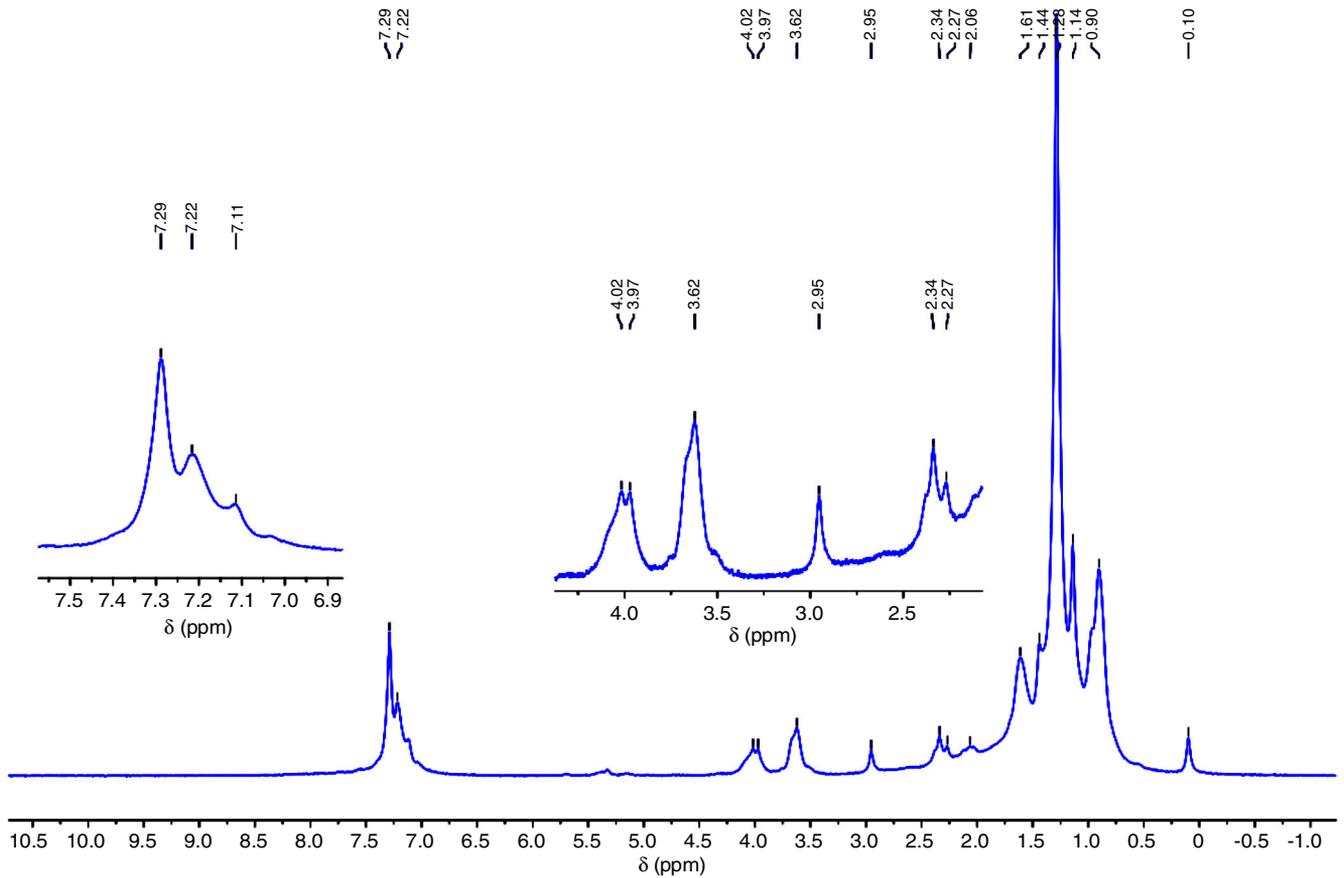
Fig. 2. ¹H NMR spectrum of the dichloromethane extract of urban aerosol sample collected in the spring season
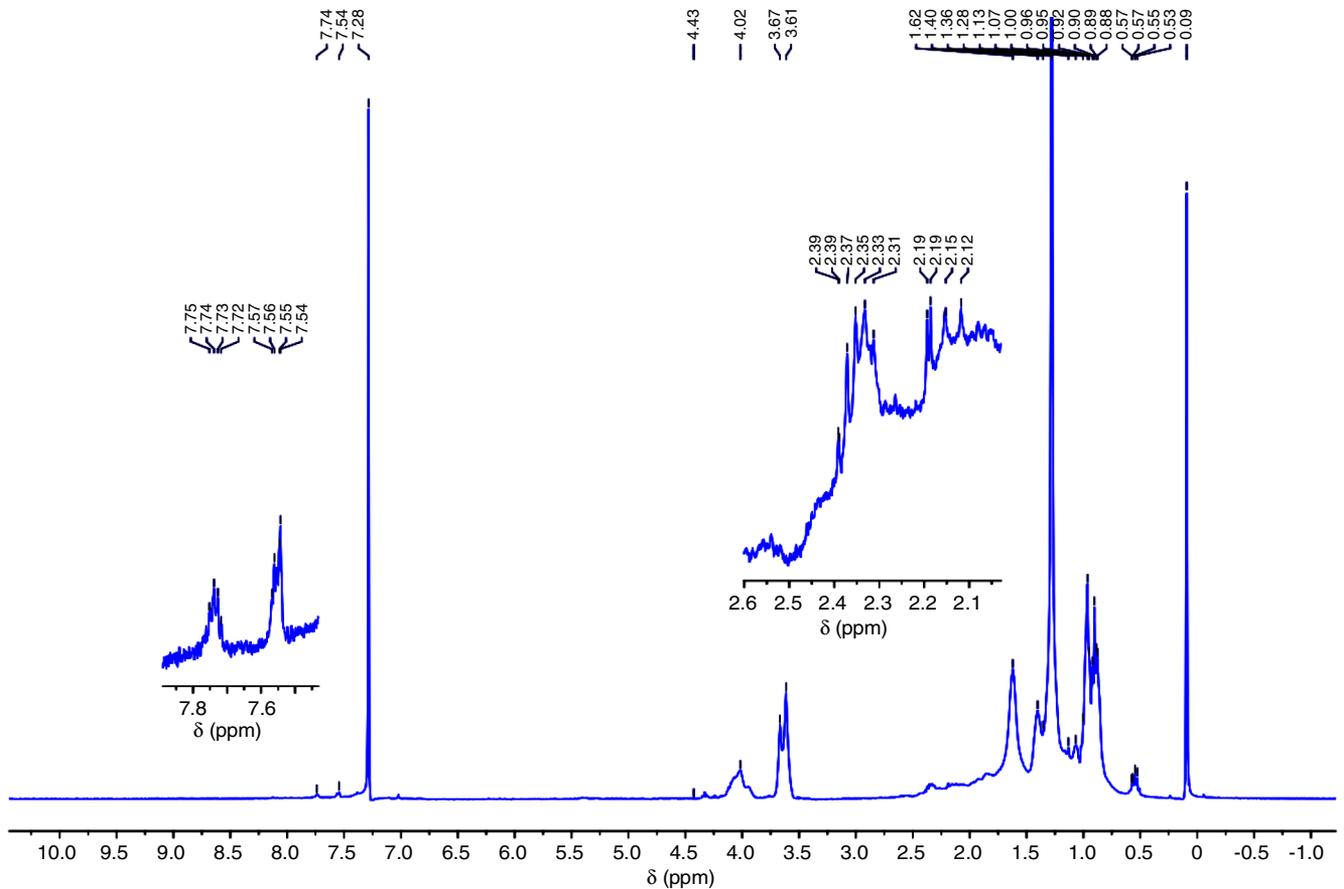
Fig. 3. ¹H NMR spectrum of the dichloromethane extract of urban aerosol sample collected in the summer season
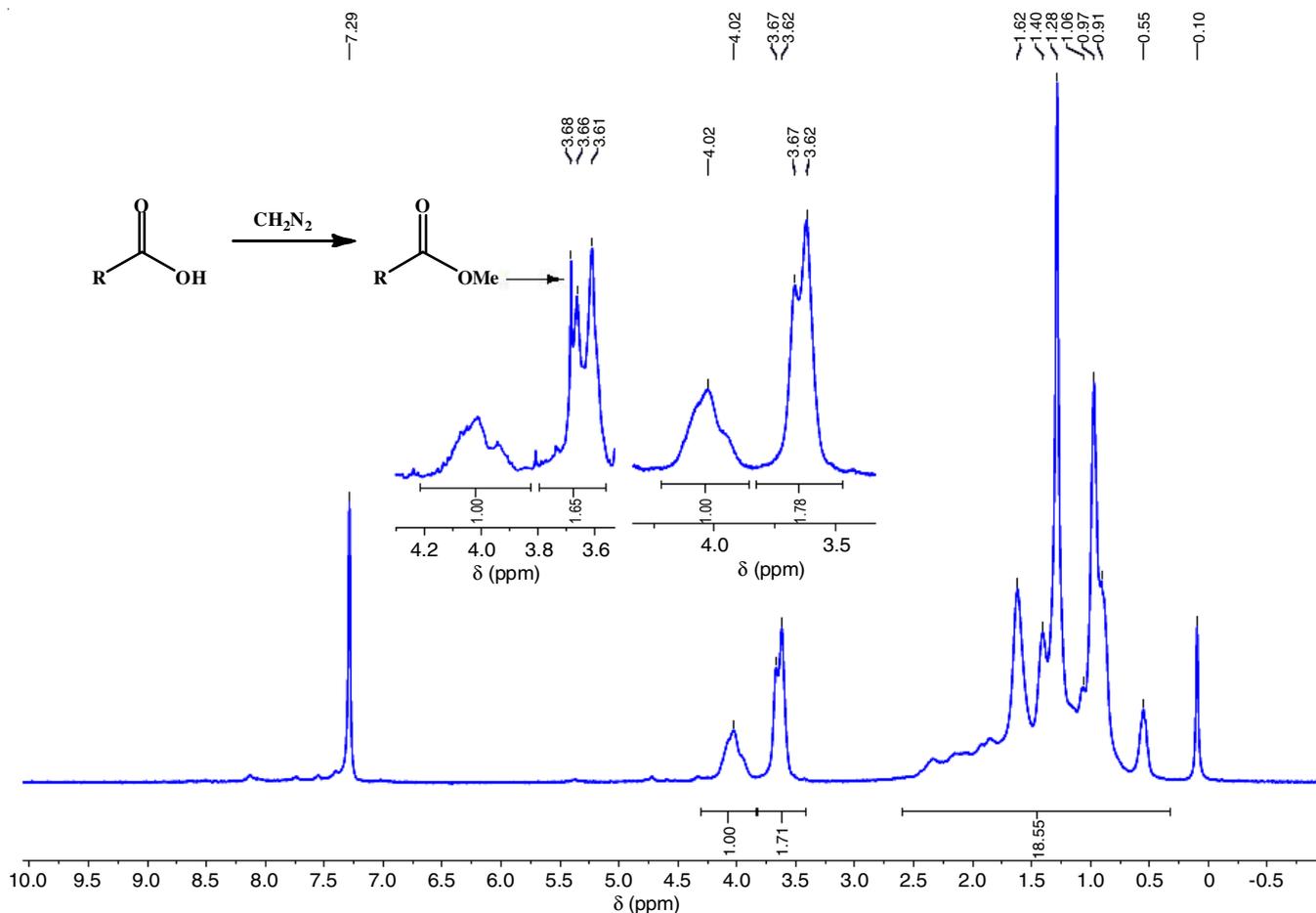
Fig. 4. ¹H NMR spectrum of the dichloromethane extract of urban aerosol sample collected in the autumn season. Chemical derivatization of aerosol sample using diazomethane (CH₂N₂)
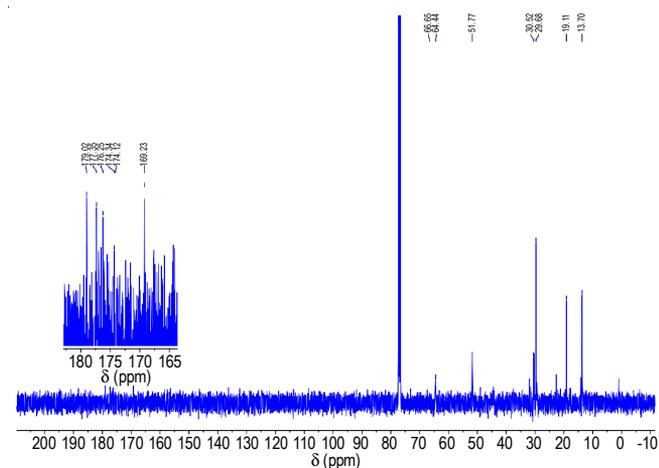
Fig. 5. ¹³C NMR spectrum of the dichloromethane extract of urban aerosol sample collected in the winter season

respectively [27,28]. Attention has been paid to the signals at 51 and 64 ppm, which we identify as signals of carbon atoms bound with nitrogen or oxygen (for example, esters or amides). The presence of esters or amides in aerosol extracts can be confirmed by weak carboxyl carbon signals in the region of 170-180 ppm.

The IR spectra of aerosol extracts are usually characterized by relatively small, wide bands and therefore look simpler than the spectra of pure substances (Fig. 1). This seeming simplicity is accounted for by the fact that aerosol extracts consist of complex mixtures of organic compounds, and therefore the characteristic bands of the obtained IR spectrum indicate the presence of a specific functional group in many components of the extract. It should be clarified that similar in appearance infrared spectra of such complex mixtures do not necessarily mean similar compounds in the composition of these mixtures [26-29].

In the IR spectrum (Fig. 6) of an extract derived from aerosol particles, a broad band is visible at 3446 cm⁻¹, which refers to the stretching vibrations of O-H bond in the phenolic, hydroxyl and carboxyl groups, as well as the stretching vibrations of bond N-H in amines and amides. Bands about 2957, 2924 and 2854 cm⁻¹ are attributed to asymmetric C-H stretch of methyl (CH₃) and methylene (CH₂) groups of aliphatic chains. Intensive band near 1730 cm⁻¹ assigned to carbonyl stretching vibrations from ketones, aldehydes and/or carboxylic acids. The weak band at 1633 cm⁻¹ can be explained by C=C stretching of aromatic rings and C=O stretching of conjugated carbonyl groups. The bond of average intensity at 1464 cm⁻¹ probably corresponds to the bending vibration of C-H bonds in alkyl fragments, whereas adsorption at 1381 cm⁻¹ can be attributed to symmetrical C-H bending vibrations from aliphatic methyl (CH₃) groups. Band 1261 cm⁻¹ can be attributed to the stretching vibration of a single C-O bond in ethers and esters. A wide band in the range of 1163-1044 cm⁻¹ can most likely be attributed to the
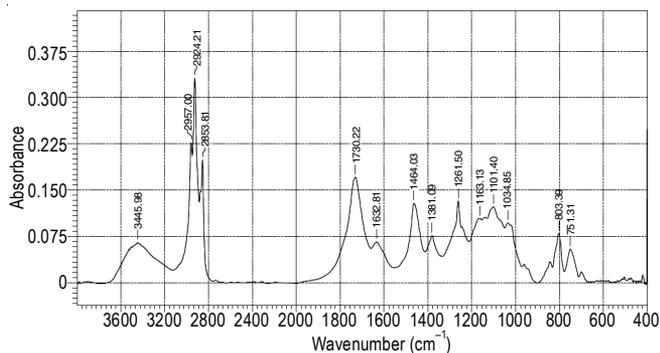
Fig. 6. FTIR spectrum of organic compound mixture isolated from dichloromethane extract of urban atmospheric aerosol

stretch vibrations of C-O bonds in the alcohols components of the aerosol extract. Adsorption peaks in the frequency range of 840-750 cm^{-1} interval may be due to C-H bending vibrations of alkene groups. However, due to different spectral absorption coefficients and sufficiently wide IR ranges, the identification of signals has a certain degree of uncertainty.

Conclusion

In this work, based on ^{1}H NMR spectral data, it was found that organic composition of PM$_{2.5}$ fraction of urban aerosols varies imperceptibly with the time of year; the maximum content of low molecular weight organic components in aerosol fraction was observed in the winter period. Comparative analysis of ^{1}H NMR, ^{13}C NMR and IR spectra showed that the main organic components of aerosol extracts are aliphatic oxygen-containing compounds (such as derivatives of carboxylic acids and esters), whereas aromatic compounds are present in small quantities. Derivatization of the aerosol extract using diazomethane confirmed the presence of aliphatic carboxylic acids.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. R.M. Silverstein, G.C. Bassler and T.C. Morril, Spectrometric Identification of Organic Compounds, Wiley: New York, edn 5, p. 430 (1991).
2. S. Takahama, G. Ruggeri and A.M. Dillner, *Atmos. Meas. Techn.*, **9**, 3429 (2016);
https://doi.org/10.5194/amt-9-3429-2016.
3. European Environment Agency, Status of Black Carbon Monitoring in Ambient Air in Europe, Technical Report Nº18 (2013).
4. E. Tagliavini, F. Moretti, S. Decesari, M.C. Facchini, S. Fuzzi and W. Maenhaut, *Atmos. Chem. Phys.*, **6**, 1003 (2006);
https://doi.org/10.5194/acp-6-1003-2006.
5. R.-J. Huang, J. Cao, Y. Chen, L. Yang, J. Shen, Q. You, K. Wang, C. Lin, W. Xu, B. Gao, Y. Li, Q. Chen, T. Hoffmann, C.D. O'Dowd, M. Bilde and M. Glasius, *Atmos. Meas. Tech.*, **11**, 3447 (2018);
https://doi.org/10.5194/amt-11-3447-2018.
6. Air Quality Guidelines, Global Update 2005, Particulate Matter, Ozone, Nitrogen Dioxide and Sulfur Dioxide, World Health Organization, DK-2100 Copenhagen, Denmark (2006).
7. E. Samoli, R. Peng, T. Ramsay, M. Pipikou, G. Touloumi, F. Dominici, R. Burnett, A. Cohen, D. Krewski, J. Samet and K. Katsouyanni, *Environ. Health Perspect.*, **116**, 1480 (2008);
https://doi.org/10.1289/ehp.11345.
8. R. Beelen, G. Hoek, P.A. van den Brandt, R.A. Goldbohm, P. Fischer, L.J. Schouten, M. Jerrett, E. Hughes, B. Armstrong and B. Brunekreef, *Environ. Health Perspect.*, **116**, 196 (2008);
https://doi.org/10.1289/ehp.10767.
9. D. Krewski, M. Jerrett, R.T. Burnett, R. Ma, E. Hughes, Y. Shi, M.C. Turner, C.A. Pope III, G. Thurston, E.E. Calle, M.J. Thun, B. Beckerman, P. DeLuca, N. Finkelstein, K. Ito, D.K. Moore, K.B. Newbold, T. Ramsay, Z. Ross, H. Shin and B. Tempalski, *Res. Rep. Health Eff. Inst.*, **140**, 5 (2009).
10. C.A. Pope III, R.T. Burnett, M.J. Thun, E.E. Calle, D. Krewski, K. Ito and G.D. Thurston, *JAMA*, **287**, 1132 (2002);
https://doi.org/10.1001/jama.287.9.1132.
11. Y.-F. Xing, Y.-H. Xu, M.-H. Shi and Y.-X. Lian, *J. Thorac. Dis.*, **8**, E69 (2016);
https://doi.org/10.3978/j.issn.2072-1439.2016.01.19.
12. X. Zhang, J. Sun, Y. Wang, W. Li, Q. Zhang, W. Wang, J. Quan, G. Cao, J. Wang, Y. Yang and Y. Zhang, *Chinese Sci. Bull.*, **58**, 1178 (2013);
https://doi.org/10.1360/972013-150.
13. E. Samoli, A. Analitis, G. Touloumi, J. Schwartz, H.R. Anderson, J. Sunyer, L. Bisanti, D. Zmirou, J.M. Vonk, J. Pekkanen, P. Goodman, A. Paldy, C. Schindler and K. Katsouyanni, *Environ. Health Perspect.*, **113**, 88 (2005);
https://doi.org/10.1289/ehp.7387.
14. D. Gao and S. Feng, F. Liao, F. Zhou, X. Wang, *Ecotoxicol. Environ. Saf.*, **128**, 67 (2016);
https://doi.org/10.1016/j.ecoenv.2016.01.030.
15. G.-Y. Lin, G.-R. Lee, S.-F. Lin, Y.H. Hung, S.-W. Li, G.-J. Wu, H. Ye, W. Huang and C.-J. Tsai, *Aerosol Air Qual. Res.*, **15**, 2305 (2015);
https://doi.org/10.4209/aaqr.2015.04.0271.
16. J. Wu, W. Xie, W. Li and J. Li, *PLoS One*, **10**, e0142449 (2015);
https://doi.org/10.1371/journal.pone.0142449.
17. An ill wind blows: The Current State and Impact of Cross-Border PM$_{2.5}$.
http://www.smfg.co.jp/english/responsibility/report/magazine/safe/pdf/safe101_2.pdf
18. R.M. Harrison, A.M. Jones and R.G. Lawrence, *Atmos. Environ.*, **38**, 4531 (2004);
https://doi.org/10.1016/j.atmosenv.2004.05.022.
19. C.A. Pope III, J.B. Muhlestein, H.T. May, D.G. Renlund, J.L. Anderson and B.D. Horne, *Circulation*, **114**, 2443 (2006);
https://doi.org/10.1161/CIRCULATIONAHA.106.636977.
20. T. Lanki, J. Pekkanen, P. Aalto, R. Elosua, N. Berglind, D. D'Ippoliti, M. Kulmala, F. Nyberg, A. Peters, S. Picciotto, V. Salomaa, J. Sunyer, P. Tiittanen, S. von Klot and F. Forastiere, *Occup. Environ. Med.*, **63**, 844 (2006);
https://doi.org/10.1136/oem.2005.023911.
21. I. Harrabi, V. Rondeau, J.F. Dartigues, J.F. Tessier and L. Filleul, *Environ. Res.*, **101**, 89 (2006);
https://doi.org/10.1016/j.envres.2006.01.012.
22. M. Paglione, S. Saarikoski, S. Carbone, R. Hillamo, M.C. Facchini, E. Finessi, L. Giulianelli, C. Carbone, S. Fuzzi, F. Moretti, E. Tagliavini, E. Swietlicki, K. Eriksson Stenström, A.S.H. Prévot, P. Massoli, M. Canaragatna, D. Worsnop and S. Decesari, *Atmos. Chem. Phys.*, **14**, 5089 (2014);
https://doi.org/10.5194/acp-14-5089-2014.
23. A.A. Uspenski and A.V. Stepakov, *Asian J. Chem.*, **30**, 1845 (2018);
https://doi.org/10.14233/ajchem.2018.21341.
24. F. Arndt, *Org. Synth.*, **15**, 3 (1935);
https://doi.org/10.15227/orgsyn.015.0003.
25. S. Decesari, M.C. Facchini, S. Fuzzi and E. Tagliavini, *J. Geophys. Res.*, **105(D1)**, 1481 (2000);
https://doi.org/10.1029/1999JD900950.
26. J.-D. Mao, L.S. Hundal, K. Schmidt-Rohr and M.L. Thompson, *Environ. Sci. Technol.*, **37**, 1751 (2003);
https://doi.org/10.1021/es020821z.
27. E.R. Graber and Y. Rudich, *Atmos. Chem. Phys.*, **6**, 729 (2006);
https://doi.org/10.5194/acp-6-729-2006.
28. R.M.B.O. Duarte, C.A. Pio and A.C. Duarte, *Anal. Chim. Acta*, **530**, 7 (2005);
https://doi.org/10.1016/j.aca.2004.08.049.
29. S. Pongpiacha, *J. Appl. Sci. (Faisalabad)*, **14**, 2967 (2014);
https://doi.org/10.3923/jas.2014.2967.2977.