# Characterization of Urban Atmospheric PM2.5 by ATR-FTIR, ICP-MS and SEM-EDS Techniques

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The study aims to investigate the chemical composition of airborne particulate matter with size below 2.5  $\mu$ m (PM2.5) collected from Targoviste City area, in the summer of 2015. For this consideration eleven representative points have been chosen for sampling. This research provides interesting data which can clarify the relationship between PM2.5 exposure and the negative effects on human health at urban area level. Three analytical techniques have been developed for the qualitative, quantitative and morphological characterization of PM<sub>2.5</sub>. The inorganic and organic functional groups of the PM<sub>2.5</sub> samples were investigated by Attenuated Total Reflectance - Fourier Transform Infrared Spectrometry (ATR-FTIR). The content of several elements (i.e. Pb, Cd, Cr, Ni, Cu, Mn, Al, Zn and Fe) in samples was determined by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). The measured concentration of these metals was compared with values reported by the International Agency on urban area in order to establish the minimal element level which cannot be considered as a potential health risk for the urban population. The morphological characterization of PM<sub>2.5</sub> was performed by Scanning Electron Microscopy - Energy Dispersive Spectrometry (SEM-EDS). The elements, such as C, O, Si, Ca, N and S.

Keywords: particulate matter, ATR-FTIR, ICP-MS, SEM-EDS, chemical composition

The study of the chemical composition of particulate matter (PM) is very important due to their negative effects on human health [1, 2]. Airborne particles exist as either solid or liquid, with diameters ranging from 0.002 to 100 μm. Particles with an aerodynamic diameter of 2.5 μm (PM<sub>2</sub>) are considered fine particles with a high risk for health. Particles with size larger than  $2.5 \,\mu m$  are classified as course particles. A number of epidemiological studies [3-9] have shown that a rise of  $PM_{_{2.5}}$  concentrations in atmosphere led to an increase of respiratory and cardiovascular diseases among the population of the planet. Also, the size of  $2.5\mu m$  and sharp as well, were used as indicators for fine particles during to researches, conducted by the American Cancer Society, in order to assess the relationship between exposure to PM25 concentrations and cancer risk. The chemical composition of PM, depends heavily by the emission source and, from this reason, a particle may contain more than one chemical species. Therefore, it is well know that the source of the particulate matter is highly important in the composition study of airborne particles. In urban areas, where are predominant industrial emissions, traffic, energy industry, domestic activities and natural emissions as well, the suspended matter has a complex composition, including heavy metals, water, inorganics and organic compounds. In rural areas, these particles arise mainly from natural sources, but there is also a moderate influence of human activities (i.e. domestic and agricultural occupations). The particulate matter contain, mainly, the following components [10-20]: ions (e.g. sulphate, ammonium, nitrate, chloride, sodium, calcium, magnesium, potassium), 20 heavy metals (e.g. Ag, As, Ba, Be, Dc, Ce, Co, Cu, Fe, Mn, Nd, Ňi, Pb, Sb, Se, Sr, Ti, V and Zn), at least 160 organic compounds, inorganics, elemental carbon,

water and components of the earth's crust. Thus, can be distinguished different particles [21, 22] which are emitted directly into the atmosphere (e.g. dust, sea salt etc.), as well as particles formed from precursor gases (i.e. those which containing sulphur and secondary organic compounds). It is well known that International Agency for Research on Cancer has classified heavy metals, especially chromium and nickel, as potential cancer agents [23-32]. Currently, there are several hypotheses [33-35] to explain the association of  $PM_{25}$  and adverse health effects.

In this research, three analytical techniques have been developed for the qualitative, quantitative and morphological characterization of PM<sub>2.5</sub> The chemical composition of particulate matter with size 2.5µm provides well information about health risks exposure. In this respect, the inorganic and organic compounds of PM<sub>a</sub>, were investigated by Attenuated Total Reflectance - Fourier Transform Infrared Spectrometry (ATR-FTIR) [36]. This analysis of the samples provided important details on the functional group composition of the PM, 5. The content of nine metals (i.e. Pb, Cd, Cr, Ni, Cu, Mn, Al, Zn and Fe) from PM<sub>25</sub> samples, collected in the summer of 2015, from eleven points of urban area of Targoviste City was determined by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). The morphological characteristics of PM<sub>25</sub> samples were performed by Scanning Electron Microscopy - Energy Dispersive Spectrometry (SEM-EDS).

#### **Experimental part**

## Site description and sampling

The sampling was carried out between June and August 2015, in eleven points of Targoviste City, being well-known that industrial activities and traffic as well, are the main causes of pollution in the city. Prior in choosing the sampling

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location, the sites (e.g. **P1-P11**, fig. 1) were evaluated based on set criteria, such as: representativeness of the sampling site for the rest of the city (e.g. proximity of kindergartens, schools, hospital, health centers, and university campus), usually pollution sources (traffic, industrial and domestic activities) and in site security (the opportunity to make measurements for a period of 24 h).



Fig.1. Location of sampling points in Targoviste City and surroundings

Samples were collected in accordance with EMEP manual for sampling and chemical analysis [37] as well as the sampling methods presented in several studies [38, 39], slightly modified. An environmental monitoring system by Casella was used to achieve the measurements in order to PM<sub>2.5</sub> characterization. The filters used for sampling were weighted (mean of tree weights) until to a standard deviation of 0.00002 g, and then were stored in Petri dishes and kept in desiccators until the conditioning process was achieved. After 24 hours sampling period, each filter sample were stored at -20 °C before analysis. In order to avoid contamination, all filters were handled with Teflon forceps and powder-free Teflon gloves.

### Materials

All chemical reagents were of analytical grade. Distilled deionized water (Milli-Q Water System Millipore, USA) was used throughout. Also, nitric acid (high purity, Merck) was used for the blank preparation (1 % nitric acid) and digestion process.

# Analytical techniques

Molecular identification of chemical functional groups of inorganic and organic compounds deposited on filters was performed by Attenuated Total Reflection - Fourier Transform Infrared spectrometry (ATR-FTIR) using Vertex 80v spectrometer (Bruker), which adsorbs infrared radiation in 600-8000 cm<sup>-1</sup> range and equipped with diamond ATR crystal accessory, for high refractive index bulk sample, as well as with HYPERION microscope. ATR-FTIR spectrometry has limited applications in quantitative researches, since it has a penetration depth of only a few microns, but for qualitative investigation could be a suitable technique. ATR-FTIR method did not required special preparation of samples. The blank was handled exactly as each sample filter from pre-scan until the final analysis was completed.

The analysis and quantification of trace elements, including Cu, Pb, Zn, Cr, Cd, Al, Ni, Fe, and Mn, in liquid mineralized samples were performed by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) by using iCAP<sup>TM</sup> Qc device. For ICP-MS analysis, the samples were digested with 9 mL HNO<sub>3</sub> on a hot plate by using a TOPwave Microwave-assisted pressure system. After digestion process, the PTFE-TFM vessels with samples were cooled for 1 hour, and then the solutions were

transferred with distilled water to 25 mL volumetric flasks. Finally, the clear solution samples were analyzed by ICP-MS. The quantification of this technique was performed by a standard curve procedure. Metals calibration curves showed good linearity over the concentration range (0.1 to  $10.0 \text{ mg L}^{-1}$ ), with R<sup>2</sup> correlation coefficients in the range of 0.995 to 0.999. The analytical curves for each analyzed elements were prepared using a stock standard solutions (Merck). The LODs of analyzed elements were established using the calibration data. The measurements were performed in triplicate mode. Standard reference material (i.e. NIST SRM 1648a, *Urban Particulate Matter*) was used to verify the accuracy and traceability of the method. The relative standard deviation was determined, as well. The recovery rate was in the range of 94.2-101.5%.

The morphological characterization of PM, was performed using scanning electron microscope (SEM) SU-70 Hitachi, coupled with UltraDry energy dispersive X-ray spectrometer (EDS). SEM-EDS analysis has not required special treatment of samples.

# **Results and discussions**

In this study, the morphology and chemical composition of  $PM_{2.5}$  samples collected from Targoviste City, in the summer of 2015, were investigated by different analytical techniques. Therefore, ambient samples were qualitatively analyzed using ATR-FTIR spectrometry, an ideal nondestructive method for investigation the inorganic and organic functional groups, such as  $CO_3^{-2}$ ,  $NH_4^+$ ,  $SiO_4^{-2}$ ,  $NO_3^-$ , carbonyl and aliphatic carbons. The identified groups (table 1) were selected due to their commonality to airborne  $PM_{2.5}^$ and well-known pollution sources. In table 1 several weak, medium and strong peaks, marking the presence of different functional groups, assigned as follows:  $SO_4^{-2}$  (612-617 cm<sup>-1</sup>),  $NO_3^-$  (820-840 cm<sup>-1</sup> for all eleven points, and 1350-1359 cm<sup>-1</sup>, value identified only in P6 point),  $SiO_4^{-4}$ (777-794 cm<sup>-1</sup> and 1035 cm<sup>-1</sup>),  $CO_3^{-2-}$  (871-885 cm<sup>-1</sup> and 1450 cm<sup>-1</sup>),  $NH_4^+$  (1410-1412 cm<sup>-1</sup> and 3019-3040 cm<sup>-1</sup>), carbonyl group, C = O (1640-1645 cm<sup>-1</sup>), aliphatic carbon, C-H (1455 and 2919-2937 cm<sup>-1</sup>) and alcohols, C – OH, (3310-3358 cm<sup>-1</sup>).

The minimum, maximum and average concentration of elements (i.e. Cu, Pb, Zn, Cr, Cd, Al, Ni, Fe and Mn) in PM<sub>2.5</sub> samples (N=99) are shown in table 2 and figure 2. All metals were detected in collected material. From collected data, it was obvious that Fe was the most enriched metal in PM<sub>2.5</sub>, followed by Zn > Mn > Ni >Cu >Al > Pb > Cr > Cd. The results indicate that iron is one of most easily released elements into the suspended particles, and the mainly source is given by the industrial activities (i.e. **P10**). Furthermore, for each metal, the concentration largely varied between selected sites.

The average content of lead (table 2 and fig. 2a) ranged from 6.80 ng/m<sup>3</sup> in **P5** (automobiles and railway traffic, comercial and domestic fuel combustion, industrial activity, being one of the main entrances of the city) to 4.30 ng/m<sup>3</sup> in P3 site coresponding to University campus. Instead, the presence of lead in **P10** sampling point is certainly due to traffic and industrial activity. These high values are obtained in August 2015, one of the hottest month of the year. The average of cadmium concentration (table 2 and fig. 2b) was higher in **P1**, such as 1.20 ng/m<sup>3</sup> (intense industrial activity, automobiles and railway traffic, commercial, and residential heating), and lower in **P8** (residential district), such as 0.60 ng/m<sup>3</sup>. Cadmium occurs in air particles as inorganic/organic soluble or insoluble salts. The average of chromium content (table 2 and fig. 2c) for sampling points collected from Targoviste City ranged between 2.88

Table 1INFRARED SPECTRAL DATA OF ORGANIC AND INORGANIC COMPOUNDS FROM  $\mathrm{PM}_{2.5}$  SAMPLES

Sample	ATR-FTIR spectrometry								
	Wavenumber [cm <sup>-1</sup> ]	Relative Intensity							
	June 2015								
P1	3358/3022/2967/1645/1455/1413/1035/871/840/794/613/	w/w/w/m/w/m/s/m/w/w/w/							
P2	3310/3019/2960/1642/1453/1410/1035/880/833/793/614/	w/w/w/m/w/m/s/m/w/w/w/							
P3	3350/3031/2942/2150/1640/1455/1410/1036/891/836/794/	w/w/w/w/m/m/s/m/w/w/w/							
	617/								
P4	3032/2165/1642/1410/1037/887/833/777/619/	w/w/m/m/s/m/w/w/w/							
P5	3331/3021/2950/2166/1645/1412/1035/873/840/777/612/	w/w/w/w/m/m/s/m/w/w/w/							
P6	3340/3038/2955/2163/1644/1410/1350/1035/874/838/781/	w/w/w/w/m/m/w//s/m/w/w							
	619/	/w/							
<b>P</b> 7	3030/2951/1645/1452/1413/1033/877/794/712/612/	w/w/w/w/m/m/s/m/w/w/w/							
P8	3031/2960/1645/1413/1035/877/819/772/617/	w/w/w/m/m/s/m/w/w/w/							
P9	3037/2967/1645/1413/1035/877/816/779/615/	w/w/w/m/m/s/m/w/w/w/							
P10	3342/3040/2950/2167/1645/1454/1413/1357/1034/874/832	w/w/w/w/m/w/m/w//s/m/w							
	/776/718/615/	/w/w/w/							
P11	3358/3022/2962/1645/1413/1108/1035/877/794/615/	w/w/w/m/m/w/s/m/w/w/w/							
July 2015									
P1	3357/3032/2965/1644/1455/1415/1033/875/834/792/715/6	w/w/w/m/w/m/s/m/w/w/w/							
	14/	w/							
P2	3310/3039/2960/1643/1450/1412/1034/885/832/824/783/6	w/w/w/m/w/m/s/m/w/w/w/							
	16/	w/							
P3	3351/3031/2942/2150/1640/1455/1410/1036/891//831//94/	w/w/w/w/m/m/s/m/w/w/w/							
<b>D</b> 4	/16/616/ 2021/21/5/11/5/4/1415/1025/007/0220/770/615/								
P4	2921/2165/1644/1415/1035/887//820/779/615/	w/w/m/m/s/m/w/w/w/							
P5 P6	3330/3021/2950/2165/1046/1412/1035/8/3/824/77/7612/ 2262/2020/2052/2162/1645/1411/1252/1024/874//820/788/	w/w/w/w/m/m/s/m/w/w/w/							
PO	5302/3029/2952/2102/1045/1411/1555/1054/874//859/788/	W/W/W/W/m/m/W//s/m/W/W							
D7	019/ 2024/2052/1646/1452/1414/1025/077/040/704/612/								
17 D9	2924/2933/1040/1432/1414/1033/87/7840/794/012/								
10 P0	2933/2931/1048/1413/1035/877/834/822/017/	w/w/w/m/m/s/m/w/w/w/							
P10	3340/3037/2052/2160/1644/1454/1413/1350/1034/874/832	W/W/W/m/m/s/m/W/W/W/							
110	/776/712/613/	w/w/w/w/m/w/m/w//s/m/w							
P11	3350/3030/2961/1651/1413/1118/1035/877/834/794/612/	w/w/w/m/m/w/s/m/w/w/w/							
	August 2015								
P1	3341/3032/2967/1651/1455/1414/1034/871/794/791/613/	w/w/w/m/w/m/s/m/w/w/w/							
P2	3321/3039/2960/1649/1453/1427/1035/880/836/798/612/	w/w/w/m/w/m/s/m/w/w/w/							
P3	3347/3031/2942/2140/1654/1435/1410/1036/891/794/776/	w/w/w/w/m/m/s/m/w/w/w/							
	616/								
P4	2925/2165/1642/1420/1037/887/777/718/615/	w/w/m/m/s/m/w/w/w/							
P5	3350/3029/2950/2165/1645/1412/1035/876/841/773/612/	w/w/w/w/m/m/s/m/w/w/w/							
P6	3324/3038/2955/2164/1644/1410/1359/1035/874/788/711/	w/w/w/w/m/m/w//s/m/w/w							
	615/	/w/							
<b>P</b> 7	2920/2851/1643/1452/1433/1033/877/794/712/612/	w/w/w/w/m/m/s/m/w/w/w/							
P8	2932/2860/1640/1428/1035/878/817/772/616/	w/w/w/m/m/s/m/w/w/w/							
P9	2939/2867/1645/1434/1035/880/820/779/615/	w/w/w/m/m/s/m/w/w/w/							
P10	3325/3033/2950/2167/1645/1464/1419/1358/1035/879/832	w/w/w/w/m/w/m/w//s/m/w							
	/785/717/614/	/w/w/w/							
P11	3339/3032/2962/1644/1440/1128/1034/877/824/772/613/	w/w/w/m/m/w/s/m/w/w/w/							

s-strong; m-medium; w-weak.

	Рb	Cđ	Cr	Ni	Cu	Mn	A1	Zn	Fe
Minimum	4.30	0.60	0.68	4.60	4.90	12.80	2.90	33.90	75.90
Maximum	6.80	1.20	2.88	9.80	9.10	23.80	5.50	89.90	107.80
Average	5.42	0.92	1.59	6.67	6.97	19.14	3.83	67.49	92.49
Standard deviation	0.85	0.05	0.05	0.67	0.52	1.02	1.37	3.28	4.77





ng/m<sup>3</sup> in **P10** (high anthropogenic stationary point sources - metal smelter, metal treatment and coating, commercial, and residential heating) and 0.68 ng/m<sup>3</sup> in  $\mathbf{P4}$  (only traffic, domestic activity, residential heating). The chromium amount in analyzed samples was higher than expected values, according with data presented in several studies [29, 40]. The average of nickel concentration (table 2 and fig. 2d) ranged between 9.80 ng/m<sup>3</sup> in **P10** (industrial area) and 4.60 ng/m<sup>3</sup> in **P8** (residential district). Copper is an indicator of industrial activities from direct emissions, traffic and from re-suspended road dust. The average airborne copper content (table 2 and fig. 2e) ranged between 9.1 ng/m<sup>3</sup> point **P10** (industrial site) and 4.9 ng/m<sup>3</sup> in **P4** point (residential area). These data were lower compared to the average copper content in air samples of U.S. which ranged from 0.02 to 10.00µg/m<sup>3</sup>. The average concentration of manganese (table 2 and fig. 2f) in PM<sub>2</sub>

estimated to range between 23.80 ng/m<sup>3</sup> in **P10** industrial site and 12.80 ng/m<sup>3</sup> in **P4** residential district. These values of manganese obtained in the city area were higher than the ones obtained in California urban area during the five years of observation [29, 40]. Aluminium is an elemental indicator for mineral dust from wind-blown soil, wear of road pavement and construction activities. The presence of aluminium in collected samples can be attributed to the aluminium oxide, and the significantly increased values mainly occur in **P10** as a result of resuspended road dust. The average airborne aluminum content (table 2 and fig. 2g) ranged from 5.50 ng/m<sup>3</sup> (i.e. **P10**) to 2.90 ng/m<sup>3</sup> (i.e. **P4**). The average of zinc concentration ranged (table 2 and figure 2h) from 89.90 ng/m<sup>3</sup> corresponding to **P10** to 33.90 ng/m<sup>3</sup> for **P4** site. Iron oxide in PM<sub>2.5</sub> samples can originate from several sources such as: vehicle and brake wear, resuspension of road dust as well as industrial activities in

both **P10** and **P6** points. In conclusion, the presence of iron oxide in  $PM_{2.5}$ , similar with aluminium oxide, is higher in industrial areas as a result of direct emissions. Therefore, the average concentration of iron (table 2 and fig. 2i) in studied urban area was high in **P10** point (i.e. 107.80 ng/m<sup>3</sup>), an expected value due to the intense industrial activity correlated with traffic and fuel combustion as well. The low value (i.e. 75.90 ng/m<sup>3</sup>) was observed in **P4** point.

# Morphological structure of samples on different magnification order

In figure 3, at high magnification order, were observed the smaller particles which were attributed to PM<sub>9.5</sub>, being counted and measured. From SEM-EDS images (fig. 3ccomparative with blank sample fig. 3a-b) was observed that adsorbed dust particles have presented different size and, in patches, particles clusters, possible, due to the atmospheric humidity or a high degree pollution. Regarding the morphologies observed in collected material, the PM, could be divided in two significant groups: in the first one were the particles that presented a regular morphology, with characteristic facets observed in crystalline materials, associated with natural sources (i.e. suspended dust from earth's surface, P3 sample); in the second one can be included particles with spherical and spheroidal shapes, which some of them present surface defects (e.g. porosity), associated with anthropogenic sources (fig. 3c-j, excepted blank sample).

The EDS analysis reported that the most abundant elements in PM<sub>2.5</sub> were C, Si, Ca, O and S (% concentration). Also, Mg, Al, Na and K were detected in samples, but cannot be quantitative determined by EDS analysis, due to the less concentrations (<0.01%). From this point of view, these elements were determined by ICP-MS. The size of the particles from second group, less than 2.5 $\mu$ m, was observed in all sampling points (fig. 3), being associated, mainly, with exhaust emissions from traffic, commercial and industrial activities and one could say that these particles are rich in C, O, S and Si (table 3). Also, the particles with high porosity can be attributed to the presence of SO<sub>x</sub> gases resulted from combustion process (e.g. traffic, industrial and commercial activities).

The morphology and abundance of the particles found in **P10**, **P5**, **P1** and **P3** from collecting points can be explain by a great pollution in these sites, and default an associated risk on the human health. Also, the spherical morphology of the particles can be associated with the iron levels, characterized probably, by Fe-Ca-O rich, according with the elemental analysis (i.e. ICP-MS). The regular morphology (prismatic, cubic etc.) of the particles from the first group can be explained by the presence of Si, Al, O and Ca, which are originating from natural and anthropogenic sources (e.g. SiO<sub>2</sub>, CaCO<sub>3</sub> and CaSO<sub>4</sub>, the



Fig. 3. SEM images of: (a) and (b) - blank filter fiber; (c) and (d) - filter sample collected from Targoviste City - P10 industrial area (e.g. images of dust particles with 2.5 μm diameter or less, adsorbed on filter surface); (e) and (f) filter sample collected in P5 point the main entrance to the city from Bucharest; (g) and (h) filter sample collected in P1 point (industrial and commercial activities, traffic etc); (i) and (j) filter sample collected in P3 point (university campus, out of Targoviste city); the SEM images were recorded at x7000 and x12000 magnification order

Sample	Element wt. [%]								
	С	0	Si	S	Ca	N			
P1	42.43 ±0.21	34.10 ±0.14	7.84 ±0.04	3.13 ±0.02	$10.21 \pm 0.08$	2.29 ±0.02			
P2	41.89 ±0.23	36.98 ±0.12	8.73 ±0.03	$2.45 \pm 0.02$	7.80 ±0.06	2.15 ±0.02			
P3	45.26 ±0.19	32.26 ±0.11	6.84 ±0.03	$2.02 \pm 0.03$	11.40 ±0.09	2.22 ±0.01			
P4	45.13 ±0.20	32.29 ±0.13	6.54 ±0.03	$2.85 \pm 0.02$	11.02 ±0.09	2.17 ±0.02			
P5	39.67 ±0.15	40.45 ±0.14	9.92 ±0.04	3.89 ±0.03	3.22 ±0.02	2.85 ±0.03			
P6	45.23 ±0.18	33.22 ±0.14	6.64 ±0.05	2.58 ±0.03	$10.02 \pm 0.08$	2.31 ±0.02			
P7	41.24 ±0.17	36.76 ±0.15	6.88 ±0.04	$2.08 \pm 0.02$	$10.90 \pm 0.08$	2.14 ±0.02			
P8	42.19 ±0.18	36.12 ±0.17	7.04 ±0.05	$2.13 \pm 0.02$	$10.24 \pm 0.08$	2.28 ±0.02			
P9	41.79 ±0.15	35.81 ±0.12	7.59 ±0.05	$2.65 \pm 0.02$	$10.00 \pm 0.08$	2.16 ±0.03			
P10	39.48 ±0.13	40.92 ±0.11	8.45 ±0.04	$2.56 \pm 0.03$	5.78 ±0.03	$2.81 \pm 0.01$			
P11	42 07 +0 22	37 21 ±0 10	7 19 +0 04	$2.07 \pm 0.03$	936+0.05	$210 \pm 0.01$			

Table 3ELEMENTALCOMPOSITION OFPM2.5COLLECTED FROMARGOVISTE CITY, INAUGUST 2015

latter produced by the chemical reaction between CaCO<sub>3</sub> and SO<sub>2</sub> occurring during the combustion of heavy fuels).

### Conclusions

The chemical composition of PM<sub>2.5</sub> provides relevant data regarding to epidemiological assessment of regional exposures and emission sources. ATR-FTIR analysis of the PM<sub>2.5</sub> samples reveals important details about the inorganics and organic group of the airborne particles. The hazards of toxic metals for human health are well known. Considering the carcinogenic risk of several elements including Pb, Cd, Cr, Ni, Cu, Mn, Al, Zn and Fe, it was determined the contents by ICP-MS. The PM<sub>2.5</sub> samples investigations using SEM-EDS provide significant data regarding the morphology, size, crystalline form, elemental composition, and pollution sources.

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