Peculiar pollutants in the Moscow atmosphere in winter period: gas chromatography-high resolution time-of-flight mass spectrometry study

Moscow, Russia is one of the most populated cities in the world, with the metropolitan population reaching 12 million people. Moscow being also an important industrial center has several power plants, multiple industrial factories, waste incinerators, and even an oil refinery, which all contribute to air pollution. Also, one of the main sources of air pollution involves traffic. All these factors contribute to appearance of different classes of environmental pollutants. Regular monitoring of the environmental pollution is a common practice nowadays in many cities and countries. Usually, the so-called priority pollutants (US EPA 2012) are detected and quantified on a regular basis during those monitoring activities. However, with the social and economic changes around us, the environment is also changing and new, not previously reported, pollutants are appearing.

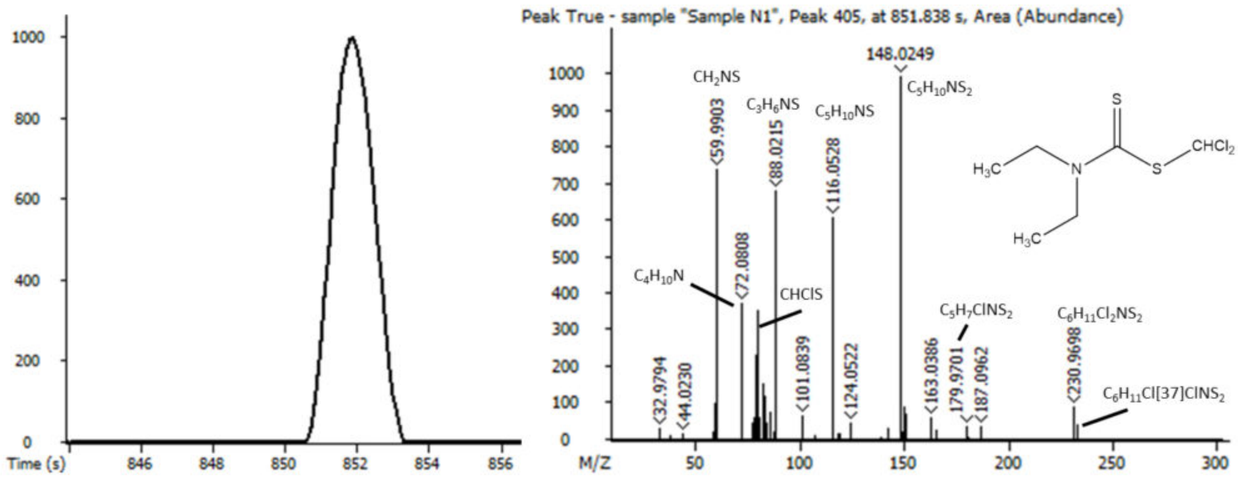

Fig. 1. The reconstructed ion chromatogram plot for m/z 230.9704 (left) and Peak True mass spectrum of the compound with an RT 851.8 s in the snow sample with elemental compositions of most important ions (right). The proposed structure of the analyte – dichloromethyl N,N-diethylcarbamodithioate ($C_6H_{11}Cl_2NS_2$) is shown on the spectrum plot.

The most common mass spectrometry approach analyzing contamination of the environment deals with targeted analysis. However non-targeted analysis is becoming more often the method of choice for the environmental chemists. It involves implementation of the modern analytical instrumentation allowing for comprehensive detection and identification of the wide variety of compounds present in the sample, such as pharmaceuticals and their metabolites, musks, disinfection by-products, flame retardants, personal care products, and many others emerging contaminants.

Snow being a good preserving matrix can capture and hold a large variety of organic compounds, even rather unstable ones. Thus, the analysis of snow collected just right before the active melting period allows evaluation of the long term air pollution in the winter period. Gas chromatography – mass spectrometry (GC- MS) is the method of choice when the main interest is focused on semi volatile compounds. GC-MS identification of knowns and structural elucidation of unknowns becomes considerably more reliable if complemented by accurate mass measurements. The accurate mass data becomes especially important when implementing “manual” identification of the analytes by using well described rules of fragmentation of organic molecules in electron ionization mode. For this reasons we used gas chromatograph coupled to high resolution time-of-flight mass spectrometer (GC-HRMS) from LECO to investigate unknown organic compounds in snow samples collected in Moscow in March 2016.

Each snow sample was placed into a 3 L glass container, melted at room temperature and then filtered through a paper filter. Further sample preparation was done according to the US EPA Method 8270. The concentrated basic and acidic dichloromethane extracts were combined before GC-HRMS analysis.

We report the presence of several new, previously not discussed, pollutants in the Moscow snow, accumulated during winter period of 2016. One example of such identification is given below.

The most probable molecular ion (m/z 230.9698) of the compound eluting at the RT 851.8 s (Fig. 1) indicates the presence of two chlorine atoms, because of relatively high intensity of [M+2]. Accurate mass measurement gave us a suggested elemental composition of the ion as $C_6H_{11}Cl_2NS_2$. The elemental compositions of the abundant and structurally important fragment ions (Fig. 1) were also well matching elemental composition of the proposed molecular ion. The main fragment ions could be well rationalized by the structure of N,N-diethylcarbamodithioic acid derivative. The key ions regarding the detailed structure consist of m/z 179.9695 ($C_5H_7ClNS_2^+$), 82.9449 ($CHCl_2^+$), and 79.9481 ($CHClS^+$). These ions indicate the presence of dichloromethyl group in the molecule next to the sulphur atom. After considering all the information the structure of the dichloromethyl N,N-diethylcarbamodithioate was proposed (Fig 1.)

The GC-HRMS method has enabled us with capability to detect and identify such peculiar analytes as iodinated compounds, polychlorinated anisoles and even Ni-containing organic complex, which are quite unexpected in environmental samples.

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