

MASS SPECTROMETRY AT ATMOSPHERIC PRESSURE: THE ANALYSIS OF THE VOLATILE ORGANIC COMPOUNDS AND SO₂

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This study focuses on the atmosphere composition and *Volatile Organic Compounds* (VOC) with mass spectrometer enabling to analyze samples in normal conditions. For this purpose, one e-nose mass spectrometer has been used to measure the gas composition of the samples collected from the center of Athens and from industrial area around Athens (about 20 km outside the city), during three months (October, November, December 2012). Three types of VOCs and sulfur dioxide are analyzed, due to their impact on the human health. The method to evaluate their concentration is based on the relative abundance. The study highlights evolution in average of the pollutant concentration in industrial and in the center of Athens; while the concentration increased in center of Athens, in the industrial area remains constant when the weather change from October to December.

Key words: pollution, VOC, gas analysis, mass spectrometry.

1. INTRODUCTION

Air pollution is a worldwide concern [1, 2, 3], a serious risk for all modern capitals, especially for those who are just emerging from industrial development. Several health risks have been associated with pollution: atherosclerosis [4], rheumatics [5], diabetes [6], intestinal disorders [7] and cardiovascular disease [8]. In spite of numerous attempts to reduce pollution [9, 10] the levels of fine particulate matter and emissions from fossil fuel combustion sources still remain the highest contributors to the atmosphere pollution.

In this respect, Athens is a suitable study case with population density of 28000 per km², near the Municipality [11], one of the most polluted cities of Europe. Due to the restrictive policies, the industry placed outside the city has no major impact,

while the traffic and the space heating emissions are the main contributors, an inventory of the air emissions showing important amounts of SO₂, CO₂, NO₂, NO, CO and VOC. In 2003, the World Calibration Center for Volatile Organic Compounds (WCC-VOC) developed a subset of 28 most important VOCs found in polluted atmosphere and responsible for smog formation [12]. Among those, propane, propylene, isoprene and benzene are commonly determined by laboratories around the world, while others like acetylenes, cyclopentanes and toluene are more difficult to assert. In addition, a significant amount of aerosols in the ambient air and indoor spaces originate from existing particles with 10-100 nm size [13]. Along VOCs, sulfur dioxide is another important pollution agent [14] responsible for bronchi-constriction and asthma, which occurs from burning fossil fuels and coal. For the evaluation and quantification of different volatile organic compounds and gaseous oxides in atmosphere, research centers use LIDAR (light detection and ranging) detection systems [15] or gas chromatography [12], olfactory instruments with the aid of a reference chamber for VOC emissions [16, 17]. E-noses have been developed in the last decade as a cheap alternative to the olfactory instruments for VOCs detection and have been applied to environment monitoring [18, 19] and components analysis in food and drinks [20, 21, 22]. Advances in E-noses are based on new technologies such as sensors array with molecular recognition, flash gas chromatography and mass spectrometry based on miniaturization of quadrupolar devices and vacuum equipment [23]. In this respect, one e-nose mass spectrometer has been engaged in the air analysis from samples collected in the center of Athens and from the industrial area around Athens (about 20 km outside the city). The atmosphere composition and VOCs are analyzed during three months (October, November, and December 2012). In addition, three VOCs are evaluated (benzene, 1,3-dimethylcyclopentane and phenol) and sulfur dioxide based on the relative abundance method. The VOCs are chosen due to the impact on human health, particularly on lungs (we selected a known aromatic compound and its hydroxygenated form: benzene and phenol — proven genotoxic carcinogens [24], a cyclic aliphatic compound: 1,3-dimethylcyclopentane — an indoor pollutant suspected to cause asthma [25] and sulfur dioxide — a major respiratory irritant).

2. METHODOLOGY

The active carbon: analytical grade grounded and sieved in the range 300-200 mesh. 50 g of active carbon are transferred in vacuumed polyethylene tubes. All the opened tubes are placed in two locations (central area and the industrial area of Athens) for one month to have an average adsorption for gases and VOCs.

These locations of central and industrial area have been chosen because there are situated in the metropolitan area and respectively in the middle of the most developed industrial site, near Athens where the pollutant concentrations have the highest values [11]. The months of October, November and December 2012 were chosen for this study in order to evaluate the evolution of pollutants crossing from warm to cold weather. The tubes are immediately capped after sampling and are prepared for analysis. In each location three collector tubes are placed.

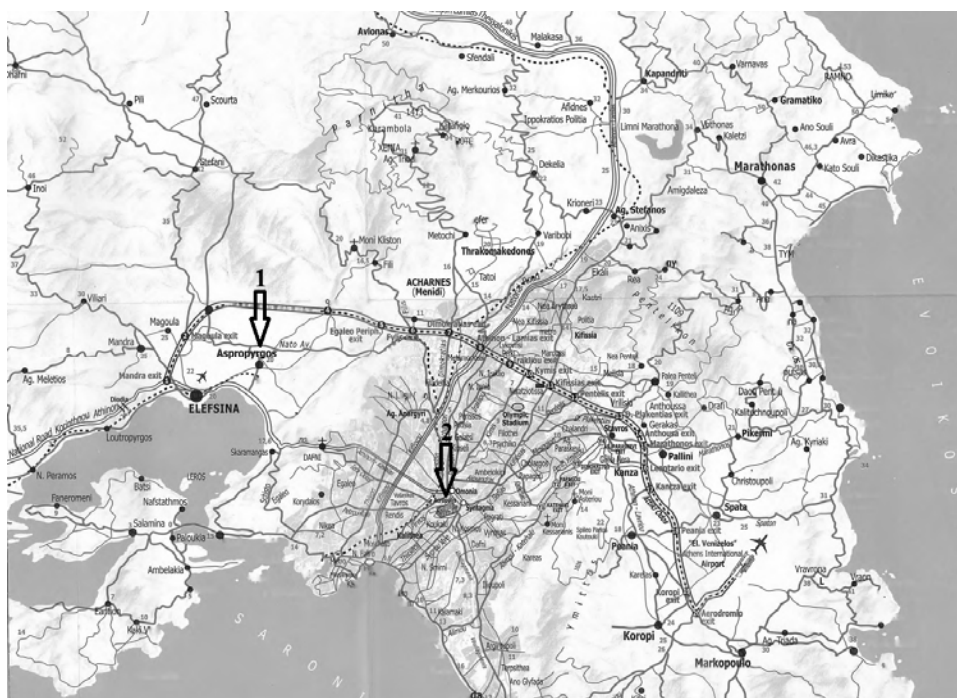


Fig.1 – The samples were collected from two areas: (1) Aspropyrgos – an industrial area located at 16 km outside Athens and (2) the metropolitan area of the center of Athens. Both areas are well known for their heavy breathing air, charged with pollutants.

The gas analysis was carried out with a quadrupole mass spectrometer (Prisma Plus QMS220, Pfeiffer vacuum technology) coupled with a sampling chamber and a capillary tube collector to transfer gases and vapors from atmospheric pressure to the spectrometer conditions ($<10^{-4}$ hPa). The capillary tube is inserted into a closed collector tube for the suction of the gases adsorbed on the active carbon. The capillary tube is heated at 150°C (to prevent condensation) and each collector tube is heated at 50°C in order to desorb the captured gases from the active carbon. The ionic current measured with a Faraday detector is proportional with the gases concentration, respectively with their abundance. The ionic current

(A) versus relative mass (amu) is counted and the values obtained for three samples from each location are averaged, based on the Quadera software for QMS220.

3. RESULTS AND DISCUSSIONS

The gas composition in the central and industrial area can be grouped in seven categories of compounds (Fig. 2): 1) carbon C1 and water vapors; 2) C2, nitrogen, oxygen, carbon monoxide (CO), nitrogen oxides (NO), hydrogen sulfide (H₂S); 3) C4, aromatics, paraffin, naphthene, COS; 5) C5, sulfur dioxide (SO₂) 6) C6, C7, benzene, VOC 7) C8-C10, benzene, toluene, xylene (BETX), VOC.

Therefore, one of the purposes of this work is to estimate the total organics and substances containing carbon existing in the atmosphere volume for a given location. The rectangular area S represents this total content:

$$S=10^4 \sum_{\substack{m=99 \\ z \\ m=45 \\ z}} \left(\frac{m}{z} * \text{ion current} \right) \quad (1)$$

where 10^4 is the increment factor (for increasing the magnitude area up to decimal values).

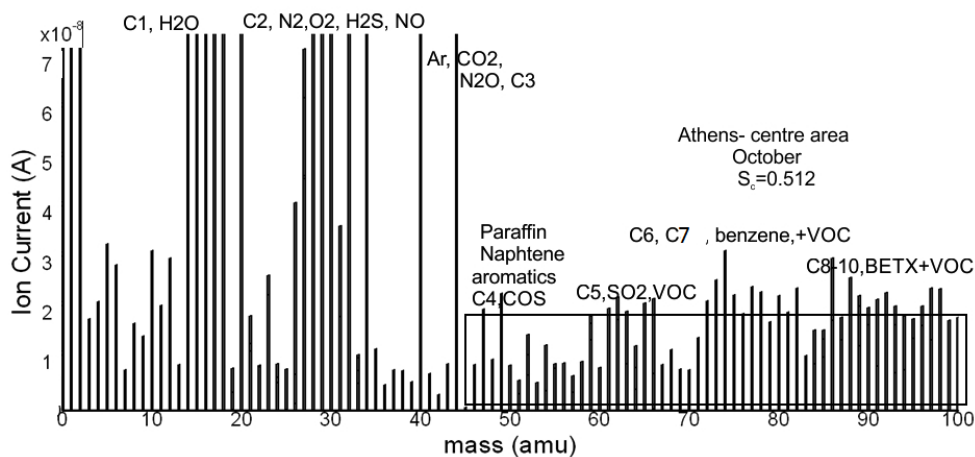


Fig. 2 – Atmospheric composition in Athens, central area. See text related to the composition.

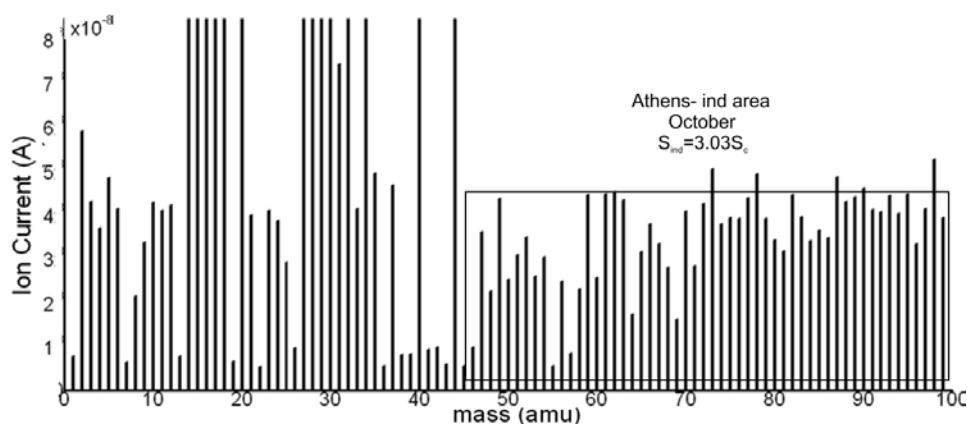


Fig. 3 – Atmospheric composition in Athens, industrial area for October.

The industrial area in October has a similar composition of atmosphere but the contribution of the pollutants (in VOCs with mass >45) is 3 times higher than in the central area (Figure 3). During November and December the pollutants concentration increases in the central area (Figure 4).

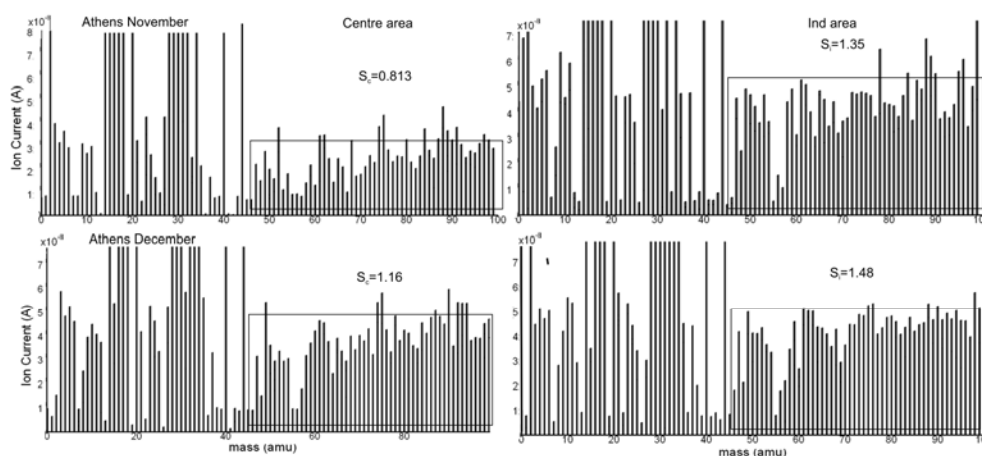


Fig. 4 – Distribution of atmospheric composition during November and December in Athens, central and industrial area.

In Table 1 the data for compounds with mass higher than 45 related with total VOCs are summarized. By comparison the atmosphere composition in the three months increases from October to December in the central area and in the industrial area it remains constant, in average. During the weather change from warmth to cold the atmosphere composition reaches almost the same level in both areas.

Table 1

Total contribution in VOCs (rectangular area, S)

Sample	Athens center, S _c	Athens ind area, S _{ind}
October	0.512	1.555
November	0.813	1.350
December	1.160	1.480

The mass spectra afford to perform a deeply analysis related to the contribution of each species in the atmosphere composition. In the industrial area, the pollution is higher than in the city area, but generally it is constant for the studied months, while in the center of Athens, it increases.

The mass spectra allow to perform a deeply analysis related to the greenhouse gases (GHG) and their abundance in atmosphere for a given location during a time interval. If it is assumed that the ion current for each species is proportional with their concentration per the sample volume therefore the total ion current as sum over all mass spectra is proportional with the average composition in the atmosphere. For given species (analyte) under electronic ionization, it takes place a specific fragmentation which can be counted from the existing database [26, 27].

The ion current as sum over all fragments per analyte is proportional with the analyte's concentration per the atmosphere volume.

Relative abundance of the each species in the atmosphere volume:

$$\text{Abundance (\%)} = \frac{\sum \text{ion current (all fragments per analyte)}}{\sum \text{total ion current}} \times 100 \quad (2)$$

This relation can be used to estimate the contribution of the pollutants in the atmosphere, to appreciate and perform analysis and comparison with other measurements [12]. The abundance of ionic masses above 45 amu is an indicator of the presence of VOCs. For instance, the abundance of three hydrocarbons (benzene C₆H₆, phenol C₆H₆O, 1, 3-dimethylcyclopentane C₇H₁₄) are examined for their impact on the malignant diseases and respectively SO₂ for the impact on the lung diseases (Figure 5). We focused to demonstrate the capability of this method, not to take into account limits and doses.

At first sight in October the abundance for the hydrocarbons in the central area is about three times lower than the abundance in the industrial area.

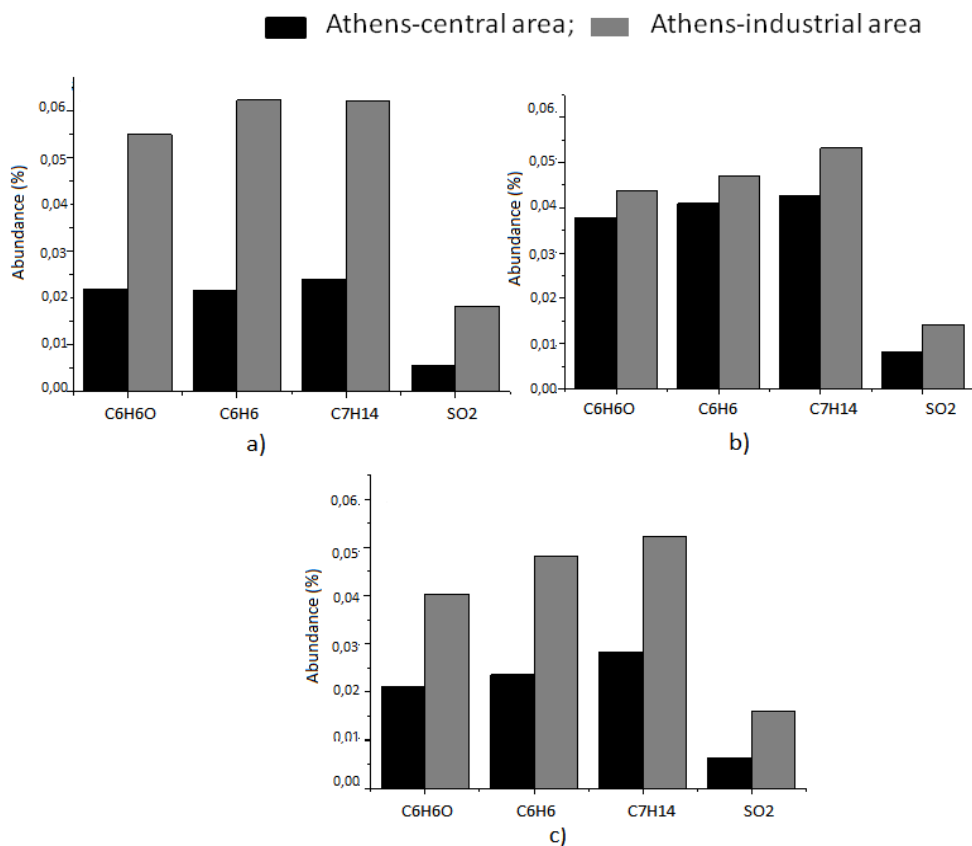


Fig. 5 – VOCs and SO₂ abundance in the industrial area and center of Athens during a) October, b) November, c) December 2012.

In November the abundance reaches at the same value in both areas and returns to the same ratio in December, as in October. The contribution of SO₂ in the atmosphere is constant during the analyzed period. The abundance of SO₂ is at least three times lower than VOC contribution. For November, the abundance of VOC in the city atmosphere grows near to the values for the industrial air, while for SO₂ the difference in magnitude for the abundance is maintained in the investigated places. In December VOCs from central area go down to October values. The abundance of benzene increases twice from October (0.02%) to November (0.04%) in the city, while for December it decreases to a value of 0.25%. In the industrial area the abundance of benzene has a maximum value in October (0.062%), a lower value in November (0.045%) and the value has a modest increase in December (0.048%). The abundance for 1,3-dimethylcyclopentane and phenol over the three studied months in the industrial area and in the city

atmosphere has the same behavior as benzene. Thus, the abundance of hydrocarbons and sulfure dioxide in the city atmosphere has the highest value in November compared with the other months. This could be the consequence of the growing number of vehicles and of the traffic conditions. The small increase of abundance in December compared to October could be a direct result of the space heating (the temperature decreased with ten degrees in December 2012 than in October).

In the industrial atmosphere, the maximum of abundance for hydrocarbons and sulfur dioxide is reached in October, while in November and December the distribution is similar; the industrial atmosphere doesn't modify its composition during November-December 2012. A possible explanation for the maximum concentration reached in October could be the industrial activity that decreased at the end of the year. However, the values of abundance for SO₂ both in central Athens and in the industrial air, are lower than the values for hydrocarbons due to several technological improvements (renewal of vehicle fleet, the use of high quality industrial filters and of catalytic technologies, high-purified fossil fuels, new age industry).

4. CONCLUSIONS

At a first glance e-nose mass spectrometry is more powerful olfactory instrument to detect and quantify complex gas composition in atmosphere.

This instrument allows to analyze the atmosphere in a given location either as global composition (based on integrated area S) or per type of analyte (deriving from the abundance). This type of data and results can be a supplementary information for the recent instruments and methods, to evaluate the atmospheric composition.

Determination of the abundance for a specific analyte correlated with the atmosphere dynamics around the city could give more accuracy in analysis.

The results obtained in this study encourage us to continue this type of measurements applied to environment monitoring, like a cheaper alternative to the olfactory instruments for VOCs detection .

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