STUDY OF PM10 PARTICLES AND DETERMINATION OF CO_2 AND CO IN AIR WITH IR SPECTROSCOPY

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Abstract: Paper is based on the determination of the main air and environment pollutants in general such as CO_2 (carbon dioxide), CO (carbon monoxide) and PM10 particles released from industrial facilities, vehicles, combustion and decomposition of dumped substances. Their impact is harmful to human health, plant and animal world. Today the world is increasingly alarmed about these risks, for human awareness of environmental protection. Physics and other sciences have given humanity the knowledge, techniques and the technology, with the application of which we extract large quantities of raw material such as minerals (fossil fuel, construction material), which are then processed to satisfy the needs of the population. But most often, the technologies used, do not take into account what is left behind the processing of raw materials and therefore industrial and other waste materials are created, which cannot be recycled in the natural exchange cycle, food chain, etc. As an illustration, according to an IPCC report of 2015 covering the energy needs of humankind in the last 100 years, during processing and use, about 400 billion tons of CO_2 are released in the atmosphere. Based on the data provided by the Metering Stations of the Ministry of Environment and Physical Planning, it shows that the high concentrations of carcinogenic airborne particles worry the citizens in many cities of the country, but not the authorities. In Skopje, Kumanovo, Tetovo, Veles and Bitola the PM10 and PM 2.5 particles concentrations are several times higher than the permissible quantities. For the determination of CO_2 and CO we have used an Infra Red spectrometer, model FT - IR (Spectrum BX FT - IR, Perkin Elmer), molecular absorption spectroscopy of laser light with wavelength 630 nm. The frequency of these rays has been applied to excite the molecular spectra of CO and CO_2 in order to determine their presence in the air as pollutants.
The measurements are focused on the spectrum range of 2075 cm-1 to 2384 cm-1. The gas samples were taken in an open environment, at several points of reference in Tetovo and Pristina, where there has been movement of vehicles during different periods of the day. The instrument is located at some reference location points in the city of Tetovo, where the instrument has been stationary from 4 to 8 hours, during this time it sucked the air constantly and then we analyzed the filters inside the instrument for particles. For the determination of PM10 particles was used PPM Systems equipment, Espoo, Finland, in accordance EN 12341: 1998. The determination is made by measuring the change in mass of the filter and clean the filter where PM10 particles were collected. For the measurement of these particles, sartorius analytical scales were used. The importance of these measurements is to explore the properties of absorption spectra and molecular structure and monitoring of environmental pollution.
Keywords: molecular spectra, pollution, monitoring, PM10 particles.

1. INTRODUCTION

Physics and other sciences have given humanity the knowledge, techniques and the technology, with the application of which we extract large quantities of raw material such as minerals (fossil fuel, construction material), which are then processed to satisfy the needs of the population. But most often, the technologies used, do not take into account what is left behind the processing of raw materials and therefore industrial and other waste materials are created, which cannot be recycled in the natural exchange cycle, food chain, etc. As an illustration, according to an IPCC report of 2018 covering the energy needs of humankind in the last 100 years, during processing and use, about 400 billion tons of CO_2 are released in the atmosphere [[i]]. Based on the data provided by the Metering Stations of the Ministry of Environment and Physical Planning, it shows that the high concentrations of carcinogenic airborne

particles worry the citizens in many cities of the country, but not the authorities. In Skopje, Kumanovo, Tetovo, Veles and Bitola the PM10 and PM 2.5 particles concentrations are several times higher than the permissible quantities [ii].

It is known that atmospheric air is polluted in different environments by industrial objects, vehicles, various combustion products and many other pollutants. Among the main pollutants of living environments and the environment in general are gases such as CO_2 (carbon dioxide), CO (carbon monoxide), SO_2 (sulfur dioxide), NO_2 (nitrogen oxide), PM10 particulate concentrations, released from industrial facilities, vehicles, burns and the decomposition of the substances being thrown away. Their impact on Humans and other organisms, for plants, is damaging to everyone, indiscriminately. Today the world is getting more alarmed about these dangers, increasing the human awareness of protecting from CO_2; CO; PM10 and other gases [iii].

Very little has been invested and done, against the biggest polluters in Pristina. While number of inhabitants and vehicles has increased, the urban expansion is still being done with the old methods, against the principles of spatial and urban policymaking. The biggest mistake is the expansion of the city on the west side, where the coal power plants "Kosova AB" and in the future "C" are operating , they count as the biggest air pollutants in the surroundings cities and Pristina.

Similar with the other cities, as well as Tetovo and Pristina, the concentration of polluting gases in those cities exceeds the allowed limit from 16 to 78 times a year [iv, v]. In the air pollution in Tetovo, Pristina and the surrounding area contribute some vehicles with internal combustion engines, considering also the type of fuel, the "Jugohrom" ore processing smelter, the textile factory "Teteks", the quarries found in the area Tetovo as well as other enterprises that produce materials for painting, facade and different farms. The biggest amount of CO_2 is released during the winter season when a lot of energy is used to heat up, and that 40% from coal and 30% from wood. From the known data taken from the measuring instruments, the most polluted cities in Macedonia are: Skopje, Tetovo, Veles and Bitola, In Kosovo the most polluted cities are considered to be the city of Prishtina, Mitrovica, Ferizaj Gjilani, Elez Han [vi, vii]. The purpose of this paper is to research some of the above-mentioned polluters in Tetovo, Pristina and certain regions. The paper includes the determination of the presence of some gaseous pollutants released in different ways in the atmosphere. For this purpose, certain points have been selected within the city of Tetovo and Pristina, which are known to have an increased level of traffic density.

2. MEASUREMENT METHOD

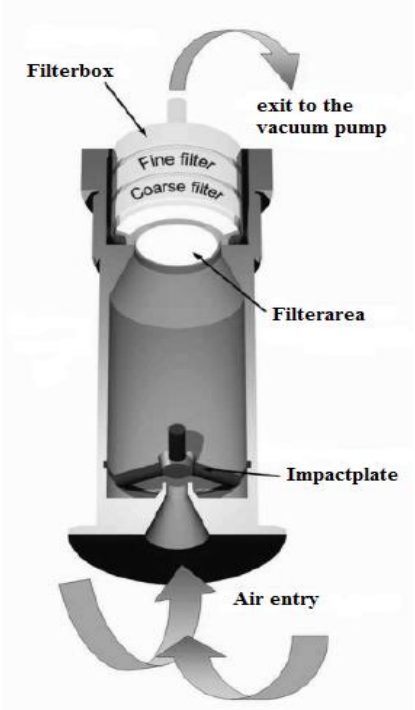

Figure 1. Sample analysis illustration with a 10μm diameter

Infrared spectroscopy is increasingly being used in the field of operational and control analysis. For the continuous measurement of the concentration of only one gas component, infrared spectroscopy is usually used for non-dispersive two-ray spectroscopy. The narrowing of the radius wavelength required for selective measurement is achieved by positive or negative filtration by selective modulation or selective emission [viii]. So, when passing electromagnetic rays through any substance, it absorbs radiation of different value wavelengths. By studying its characteristic absorption, specific data is obtained for the substance in question (Izairi, 2003) [ix], [x]. The advantages of this method compared to the classical method is that this method provides quick and complete information on the structure of the organic molecule when using very small quantities of the sample. We performed the measurements using the FT-IR Spectrometer (Spectrum BX FT-IR, Perkin Elmer). The samples taken from the various reference points were taken with a latex balloon and lastly carried in a special detection vessel.

The representation of the methodological approach to recording the amount of dust -suspension of particles up to 10 micrometers in the air of Tetovo.

The instrument is located at some reference location points in the city of Tetovo, where the instrument has been stationary from 4 to 8 hours, during this time it sucked the air constantly and then we analyzed the filters inside the instrument for particles. The instrument used in to analyze the particles is the PPM system, Espoo, Finland, was used in according to EN 12341-1998.

3. RESULTS AND DISCUSSION

The influence of automotive communication is known and it has been discussed for a long time. Here we recognize local, regional and global impacts. Local impacts are most noticeable in rural areas, such as in the City of Pristina. In addition to the polluting gases from automotive engines, we also have other impacts on the environment, for example: noise, vibration, heating, different radiation. In this paper the main point of view is the impact of polluting gases in the city of Pristina. When we talk about polluting gases, we must bear in mind the "source" of these gases. So as the main "source" of polluting gases in this region are the traffic vehicles and the coal power plants of the Republic of Kosovo. Also as a source of polluting gases during the winter season, it is worth mentioning the heating fuel in households. But mostly our measurements were made during the summer period and somehow this type of air pollution was not addressed.

As the Pristina district is a region known with its highly developed agriculture and industries, these polluting gases indirectly affect the development of the regional economy as well. Permanent monitoring of pollutant gases at a certain time was missing. For this reason, this paper is a "Pilot project" in this regard. So we had to start from the beginning by analyzing the most frequented places in the regional communication and finally detecting the polluting gasses at some points in the city of Pristina and the surroundings. Given these criteria, we decided that our points for analysis include a large part of the Pristina region, respectively at the entrance, between the city and the exit. First, the detection of the types of pollutant-polluting gases is done.

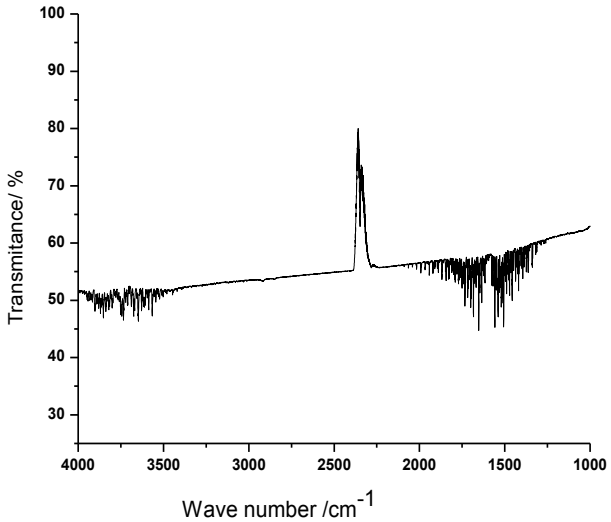

Figure 2. IR Spectrum of Carbon Dioxide in Aggregate Gas Condition

The analyzes showed that it is mainly about CO_2, CO, NOx, SO_2. Since carbon dioxide is more in the atmosphere, we decided that by spectroscopic methods (IR Spectroscopy) we could perform quantitative detection at the relevant points of Pristina and the surrounding area.

The first research is about a CO_2 (carbon dioxide) sample in Pristina.

The Asymmetric Oscillation ν_{as} (C=O) in the IR-spectrum of CO_2 is very characteristic and with high intensity and in a very peculiar position (ν = 2349 cm^{-1}). For this reason, the intensity of this band was taken as a basis for calculations. In diagram 1, the air spectrum and the characteristic band of CO_2 are clearly visible. Also seen are types of water and carbon monoxide Oscillations.

The calculation of IR Spectrum is presented in Table 1, and depicted in Figure 3. It is seen that CO_2 has a concentration of two to three times higher than the allowable value. The air pollution at the time of the measurements was relatively high. From this we can conclude that even air humidity was relatively high. Since the amount of CO in the atmosphere is extremely low, the calculation of the concentration of carbon monoxide by this method has been very problematic. In the first table, we notice the values of the CO_2 concentrations measured in five comparative points. As a comparative point we have taken the city center of Tetova: The Faculty of Agriculture (1), Faculty of Chemistry (2), The Government in the City Center (2), The Hills of the Sun (4), Hospital (5).

Table 1. *The concentration levels of CO_2 and CO in Pristina at various location points*

Position	CO_2 Concentration mg/m^3	CO Concentration mg/m^3
1	2184	0,020
2	2109	0,020
3	2437,1	0,017
4	2426	0,017
5	1502	0,028

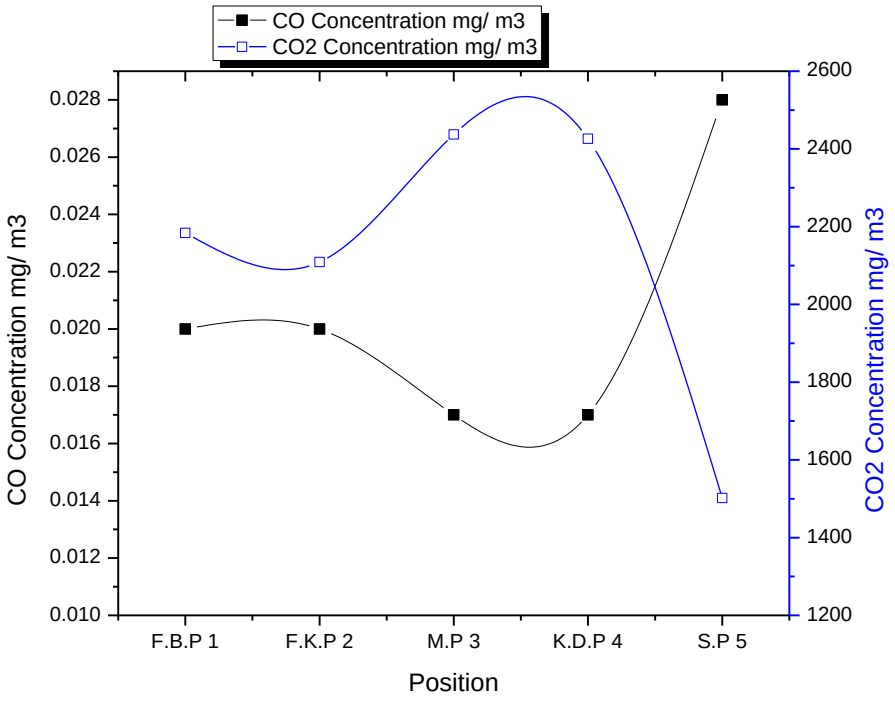

Figure 3. *The concentration levels of CO_2 and CO in Pristina at various location points.*

The second research relates to the determination of the PM10 particle concentration in some reference points in Tetovo and the surroundings

PM10 Particle measurement is done with the PPM-Systems Espoo Finland, according to ISO standards EN 12341-1998. The results of these measurements are presented in Fig.4.

Table 2. *Experimental values and comparison with the values of the Ministry of Ecology.*

Data	Position	Concentration of PM10 by Ministry of Ecology of Republic North Macedonia / μg m^{-3}	Concentration of PM10 by our team / μg m^{-3}
08.02.2018	1	103	50
09.02.2018	2	53	53
09.02.2018	3	113	16
09.02.2018	4	83	71
09.02.2018	5	110	94
23.01.2018	6	65	50

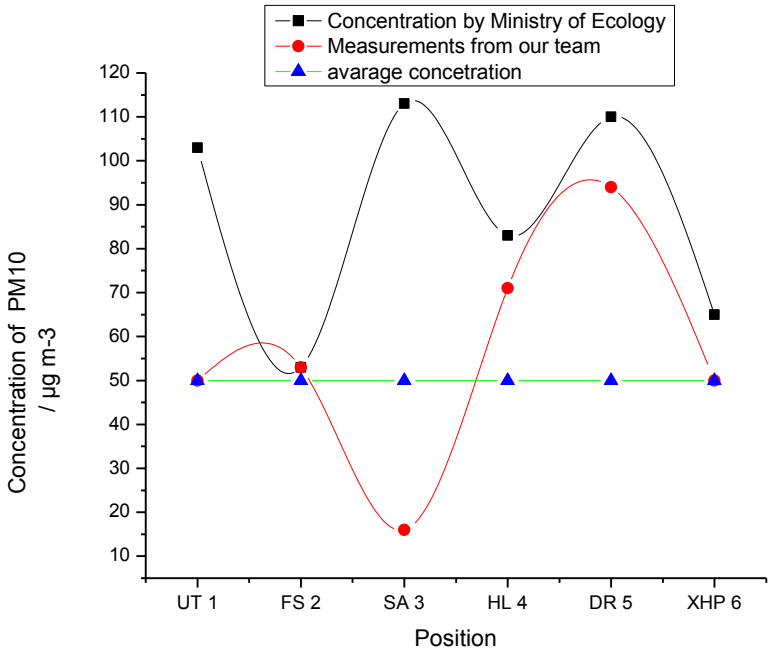

Figure 4. *The Presentation of experimental values and comparison with the values of the Ministry of Ecology.*

In the second table, we notice a difference with respect to the PM10 particulate concentrations measured in six comparative points. As a comparative point we have taken the city center of Tetova: rectorate of the University of Tetovo (1), Faculty of Mathematical Natural Sciences Tetovo (2), Tetovo bus station (3), Hotel Liraku (4), Tetovo city stadium (5), Zito Polog Tetovo companies (6). The same values are shown once again in the diagram below, Table 2, we notice that the PM10 concentration in the center of Tetovo (1) and the city stadium (2) is slightly higher compared with the lower values in the other reference points. This value contradicts the values given by the ministry of ecology, as they are higher, and these values are given by an instrument placed in a position that indicates the value for a landmark. With regard to this change, even atmospheric conditions, current air pressures, geographic position (plateau or pit) and wind speed can influence these values, as the PM10 particles are always in motion, and the vertical height that can be displaced can be two meters, these particles always move and are very close to the surface of the earth.

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