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2

Dedicated to Professor Dr. Dumitru Ristoiu
on the Occasion of His 70th Anniversary

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ON ANNIVERSARY

In 2017 the Faculty of Environmental Science and Engineering within the Babes-Bolyai University celebrates 15 years since its founding. The faculty emerged in 2002 by bringing together all the environmental education forms that existed within other faculties (Geography, Biology-Geology, Physics, Chemistry), as a result of the educational needs identified in the university. It is one of the most dynamic and modern faculties in Babes-Bolyai University and it offers study programs at bachelor, master and doctorate levels, with new, attractive and in demand specializations in the field of Environmental Science and Environmental Engineering. In time, the faculty has developed and managed to permanently adapt itself to all the priorities promoted within the educational policies and environmental strategies, trying to meet the most exigent requirements from the work market as well. The Faculty of Environmental Science and Engineering is the only faculty in the country offering study programs in this field, at bachelor, master and doctorate level.

Our faculty has a standing tradition in recognising important scientific contributions and in promoting academic values. In spirit of this tradition, we honour one of the most prominent figures of our faculty, Professor Dumitru Ristoiu.

The contributions of Professor Dumitru Ristoiu to the field of physics are remarkable, being a reputed scientists and one of the academic personalities that shaped our faculty due to his professional, scientific and managerial skills.

Between 1972 and 1991 he was employed as physician researcher in the Institute of Isotopic and Molecular Technology, Cluj-Napoca. His main activities focused on designing, developing, building, approving and space launching of the quadruplepolar KMS1 mass spectrometer and improving the equipment to the KMS 3 version and its launching on the cosmic objectives VERTICAL 9, 10 and 11. Also, he contributed to the building, designing and approval of the quadruplepolar QMS300 mass spectrometer for gas analysis.

From 1991 until 1997 he was a scientific researcher at the Babes-Bolyai University of Cluj-Napoca, studying the applications of mass spectrometry in determining Helium in gas deposits and monitoring radon through active carbon absorption.

He continued his career in the Babes-Bolyai University of Cluj-Napoca, occupying teaching positions of assistant and associate professor. His didactic fields were dosimetry, environmental radioactivity, environmental techniques and technologies, while his research interests were mass spectrometry, used energy recovery, analytic techniques for monitoring environmental pollutants. In 2005 he becomes professor in the Faculty of Environmental Science. As professor, he introduced courses such as Atmospheric physics, Unconventional energies, Applications of stable isotopes in geophysics and environment etc. and coordinated PhD. Studies in Physics and Environmental Science.

His scientific work is impressive: he has published on his own and in collaboration with various authors more than 250 scientific papers: 65 ISI papers, 39 volumes, 126 arguments and 5 books (1 as a single author – 560 pages).

Professor Ristoiu's activity, diverse and prolific in the field of physics and environmental protection, has been acknowledged ever since the beginning of his career.He has been awarded with the Gold Medal at the Exhibition of Achievements in the National Economies, USSR, Moscow, for "quadruple-polar spectrometer for space applications", authors: Ristoiu Dumitru, Kovacs Ştefan, Almăşean Mircea, Toderean Gavril, Romanţan Adriana and he received the Merit Diploma for the contribution to the development of BBU, 2004; Didactic Excellence Diploma awarded by UBB in 2006; Professor of the Year Award, 2009 and 2010; Comenius Award, 2011; Professor Emeritus Award, 2012. He is also member of numerous professional associations: Romanian Society of Physics, Romanian Society of Radioprotection, Association of Medical Physicians in Romania, Society of Scientists in Romania, European Physical Society, International Society of Indoor Air Quality and Climate, Canada, Balkan Physical Society, American Medical Physics Society, USA, "The Planetary Society", USA.

It is a very special moment for our faculty and a privilege to acknowledge here his remarkable activity and results and to dedicate professor Dumitru Ristoiu as a symbol of our highest consideration this special issue of the scientific journal *Ambientum*. On the occasion of his birthday, we have the joy to wish him Happy anniversary, much health and happiness!

On behalf of the faculty of Science and Environmental Engineering

Professor Eng. Alexandru Ozunu PhD,
Dean of Faculty of Environmental Science and Engineering

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CURICULUM VITAE - PhD Professor DUMITRU RISTOIU

Professor **Dumitru RISTOIU** was born on 26th February 1946 in Dozesti commune, Valcea county, Romania. Between 1963 and 1967 he attended the courses "Tudor Arghezi" Theoretical High School from Craiova. He then obtained a diploma in physics (atomic and nuclear physics), from the Faculty of Physics, Babes-Bolyai University of Cluj-Napoca, followed by a doctorate degree at the same institution in the field of physics, with the thesis entitled: "Study of isotopic composition of the upper Earth atmosphere using mass spectrometry" (Studiul compoziției izotopice a atmosferei superioare a Pământului folosind tehnica Spectrometriei de Masă).

Professional activity

Between 1972 and 1991 he was employed as physician researcher in the Institute of Isotopic and Molecular Technology, Cluj-Napoca. His main activities focused on designing, developing, building, approving and space launching of the quadruple polar KMS1 mass spectrometer and improving the equipment to the KMS 3 version and its launching on the cosmic objectives VERTICAL 9, 10 and 11. Also, he contributed to the building, designing and approval of the quadruple polar QMS300 mass spectrometer for gas analysis.

From 1991 until 1997 he was a scientific researcher at the Babes-Bolyai University of Cluj-Napoca, studying the applications of mass spectrometry in determining Helium in gas deposits and monitoring radon through active carbon absorption.

He continued his career in the Babes-Bolyai University of Cluj-Napoca, occupying teaching positions of assistant and associate professor. His didactic fields were dosimetry, environmental radioactivity, environmental techniques and technologies, while his research interests were mass spectrometry, used energy recovery, analytic techniques for monitoring environmental pollutants. In 2005 he becomes full professor in the Faculty of Environmental Science. As professor, he introduced courses such as Atmospheric physics, Unconventional energies, Applications of stable isotopes in geophysics and environment etc. and coordinated PhD. Studies in Physics and Environmental Science.

He has published on his own and in collaboration with various authors more than 250 scientific papers: 65 ISI papers, 39 volumes, 126 arguments and 5 books (1 as a single author – 560 pages).

There must be mentioned:

1. “Găurile” în stratul de ozon - o posibilă catastrofă climatică (“Holes” in the ozone layer – a possible climatic catastrophe), p.126-162, D. Ristoiu, in Terra - catastrofe naturale (Terra – natural catastrophes), Coordinator I. Petrescu, Editura Tehnică, Bucharest, 1993, ISBN 973-31-0515-5.
2. Ecologie – aplicații (Ecology - applications), T. Ristoiu, D. Ristoiu, UT Press, Cluj-Napoca, 2003, 161 p., IBSN 973-8335-96-5.
3. Elemente de ecologie (Aspects of ecology), T. Ristoiu, D. Ristoiu, UT Press, Cluj-Napoca, 2004, 300 p., IBSN 973-662-073-5.
4. Fizica mediului – Atmosfera (Environmental Physics – the Atmosphere), D. Ristoiu, Ed. Napoca Star, 2005, 560 pg. IBSN 973-647-268-X.
5. D. Ristoiu, C. Cosma (Coordinators and editors), Impactul factorilor fizici și bio-geo-chimici asupra dezvoltării durabile, (The impact of Physical and Bio-Geo-Chemical Factors on the Sustenable Development), Environmental and Progress, vol.6, 2006, 450 p., Editura EFES, ISSN 1584 – 6733.8

Scientific activity

Fields of interest:

- applied physics,
- dosimetry,
- environmental radioactivity,
- environmental monitoring,
- mass spectrometry,
- renewable energies.

He has published more than **250 scientific papers in these fields**.

Some examples:

- F. Copaciu, V. Coman, D. Simedru, S.M. Beldean-Galea, O. Opriş, D. Ristoiu: Determination of two textile dyes in wastewater by solid phase extraction and liquid chromatography/electrospray ionization tandem mass spectrometry analysis, Journal of Liquid Chromatography & Related Technologies, 2013, 36, 1646–1660

- M. H. Kovacs, D. Ristoiu, C. Voica: Chapter 9 Non-Invasive Matrices Use in Pollution Evaluation at Nanoscale Levels – A Way forward in Ecotoxicological Studies, pg. 167 – 184, in Novel Approaches and Their Applications in Risk Assessment, edited by Yuzhou Luo, ISBN 978-953-51-0519-0
- M. Culea, O. Cozar, D. Ristoiu: Methods validation for the determination of trihalomethanes in drinking water, Journal of Mass Spectrometry, 2006, Volume 41, Issue 12, 1594-1597
- M. Culea, O. Cozar, C. Melian, D. Ristoiu: GC/MS measurements of ambient level volatile organic compounds, Indoor and Build Environment, 2005, 14; 3-4; 241-247
- D. Ristoiu, C. Cosma, T. Ristoiu: Quadrupole Mass Spectrometer Coupled with a Membrane Inlet System, Vacuum 50(3-4), 359-362 (1998)
- C. Cosma, D. Ristoiu: Study of rare gases in geothermal waters from Herculane area, Nuovo Cimento, Geophys. Space Phys., 22, 317-323, (1999)

Documentation / Research:

Academic management:

- member in the University Scientific Research Council, BBU;
- member in the Scientific Council of Romanian Space Agency;
- 2005, he proposes a new master program: “Energy, energetic resources and the environment” (Energie, resurse energetice și mediu);
- 2006, he proposes a new master program: “Climate changes and Extreme Risk Phenomena” (Schimbări climatice și fenomene extreme de risc);
- 2003 – 2008, Director of College in Dej;
- 2009 – 2012, member in the BBU Senate.

Diplomas obtained:

- Gold Medal at the Exhibition of Achievements in the National Economies, USSR, Moscow, for “quadruple-polar spectrometer for space applications”, authors: Ristoiu Dumitru, Kovacs Ştefan, Almăşean Mircea, Toderean Gavril, Romanţan Adriana;
- Merit Diploma for the contribution to the development of BBU, 2004;
- Didactic Excellence Diploma awarded by UBB in 2006;
- Professor of the Year Award, 2009 and 2010;
- Comenius Award, 2011;
- Professor Emeritus Award, 2012.

Member of professional associations:

- Romanian Society of Physics,
- Romanian Society of Radioprotection,
- Association of Medical Physicians in Romania,

- Society of Scientists in Romania,
- European Physical Society,
- International Society of Indoor Air Quality and Climate, Canada,
- Balkan Physical Society,
- American Medical Physics Society, USA,
- “The Planetary Society”, USA.

Conf. dr. Nicoleta Bican-Brisan
CS III dr. Camelia Costan

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NATURAL RADIATION DUE TO RADON. CASE STUDY: RADON CONCENTRATION IN HOUSES FROM APUSENI MOUNTAINS

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ABSTRACT. As a radioactive decay product from rocks, in natural conditions, radon is a source of radiation for the population. Moreover, the awareness regarding the fact that this type of natural radiation is of great radiological health significance for the general population has increased since high concentrations of indoor radon were detected. The first step to prevent the risk of exposure to radon is to identify the sources and find the appropriate mitigation method. Once formed by the disintegration of heavy elements in the Earth's crust, radon diffuses into the soil and water, and then it is transported to the atmosphere. Being a noble gas, which doesn't take part in chemical reactions, radon is present in the environmental factors, such as air, water, soil and can accumulates in enclosed spaces with restricted air circulation. The aim of this paper is to determine the total amount of radon to which household members of two houses from Avram Iancu and Câmpeni (Alba County) are being exposed. The radon concentration values were within the national and international proposed limits in the field of radioprotection.

Key words: *radon concentration, soil permeability, dose, radon risk*

INTRODUCTION

An element with great mobility, formed from the decay of ^{226}Ra (a member of the ^{238}U decay chain) radon (^{222}Rn) is the most important radioactive gas because of its longest half-life of 3.82 days. This time is long enough so that a great percent of the radon atoms formed in the ground within approximately few meters from building foundation can reach the indoor environment. In some cases, radon from much larger distances than one meter can be important, if high-permeability transport routes (such as gravely soil or fissures in the ground) are available. In contrast, the thoron (^{220}Rn) formed from decay of ^{224}Ra (a member of the ^{232}Th decay chain), reaches air in substantially lesser amount because its short half-life (only 55.6 s) limits the distance that it can travel before decaying (Nazaroff *et al*., 1988).

Indoor radon exposure of important population groups and associated health risks continues to be a major issue in EU countries and in radon affected areas (Scivyer, 2007).

It is stated that from the total annual radioactive dose received by the population, over 40% is due to inhalation and ingestion of radon and its decay products (ICRP, 2012).

Research on radon concentration in buildings located in uranium mining areas where radon potential is high is of great national and international interest. In many countries authorities target monitoring all houses and implementing effective methods of reducing radon where levels are elevated (Scivyer, 2007). Moreover, several factors affecting the behaviour of radon in indoor air should be carefully studied. Radon concentration in buildings can vary widely strongly depending on the underlying geological formations and characteristics of the house, such as house structure, building materials, insulation or living habits. The main sources of indoor radon gas are represented by the soil under the house and building materials. In addition, water dissolved radon may also contribute to the levels of indoor radon (Gunby et al., 1993; Cosma and Ristoiu, 1996).

Excepting tritium, the European Commission Drinking Water Directive (98/83/EC) does not give maximum activity concentrations for individual nuclides. It sets a maximum effective dose of 0.1 mSv/y from ingestion of water from the public supply. The radon and its daughters are excluded from the calculation of this maximum effective dose. Commission Recommendation 2001/928/Euratom proposes maximum concentration values for radon (100 Bq/l) and its long-lived daughters (^{210}Po: 0.1 Bq/l and ^{210}Pb: 0.2 Bq/l). For water supply with radon concentrations above 100 Bq/l, Member States should set a reference level for radon to be used, considering also whether remedial action is needed to protect human health. A level higher than 100 Bq/l may be adopted if national surveys show that this is necessary for implementing a practical radon programme. On radiological protection grounds for excessive concentrations, exceeding 1000 Bq/l, remedial action is deemed.

Human body is exposed to radon by inhaling (Cosma et al., 2014) and ingestion. Radon is readily released from surface water; consequently, groundwater contains potentially much higher concentrations of radon than surface water.

It should be noted that radon activity concentrations in surface waters is low, usually below 1 Bq/L (EC, 2001; Ryan et al., 2003). Concentrations in ground water vary from 1 to 50 Bq/l for rock aquifers in sedimentary rocks, to 10 to 300 Bq/l for wells dug in soil, and from 100 Bq/l to 50000 Bq/L in crystalline rocks. The highest concentrations are usually associated with high uranium concentrations in the bedrock. A characteristic of radon concentrations in rock aquifers is their variability; within a region with fairly uniform rock types, some wells exhibit concentrations far above the average for that region (EU, 2001).

Study area

In order to identify radon concentration with health risk potential, two areas from Apuseni Mountains were selected as case study: Avram Iancu and Câmpeni (Alba County). Both of them belong to the North Apuseni Mountains major unit and have a different local geological setting. This fact makes possible the estimation of relation between geological setting and indoor radon concentration.

Avram Iancu is situated in the southern part of the Bihor Mountains, between the hydrographic basin of Arieșul Mic and Crișul Negru rivers. This area is characterized by the presence of uranium mineralization. The geological structure belongs to Biharia Nappe System and consists of several metamorphic rock series and un-metamorphosed mollase-type sediments with granite-granodiorite intrusions. Local geology consists of two lithological formations (ophiolitic formation in the lower part of stratigraphic sequence and calcareous-tufaceous series in the upper part of stratigraphic sequence) (Zajzon et al. 2015).

Câmpeni is located at about 25 km est of Avram Iancu to the border of Northern and Southern Apuseni Mountains. In this area surface geological deposits mainly consist of Upper Cretaceous limestones.

MATERIALS AND METHODS

Two houses were diagnosed in terms of radon potential. These were monitored by radon measurements in indoor air, radon measurements of the soil around the house and radon measurements in the water that is used in each household. For that purpose, the houses in the Apuseni Mountains area - Avram Iancu and Câmpeni, were chosen.

Radon in soil and permeability measurements

In order to determine the contribution of the soil gas to indoor radon concentration, radon in soil and the soil permeability were measured. LUK 3C radon detector equipped with Lucas cells of 145 ml was used for measuring radon in soil. This method is based on sampling soil gas and measuring the activity concentration of ^{222}Rn at non-equilibrium state with its daughters (Plch, 2012). Soil gas sampling was performed by a Janet syringe (150 ml volume) connected to a steel probe inserted in soil at 80 cm depth. The detection limit is about 1 $kBq \cdot m^{-3}$ (3σ) and the uncertainties are in the range of tens of $kBq \cdot m^{-3}$ ± 10%. Comparison measurements confirmed the results of the study in this interval (Matolin, 2010). The permeability of soil, was measured with a RADON-JOK device. The principle of determining the soil permeability k [m^2] from the emptying time t [s] is the protocol of Radon-Jok (Radon v.o.s., Czech Republic) which is based on the Darcy law (Barnet et al, 2008).

For further estimation of radon risk in a given location, radon potential of the soil (RP) can be estimated using the following expression:

$$RP = (C_{Rn} - 1) \times (-logk^{-10})$$

where: C_{Rn} [Bq/m^3] is the measured soil radon concentration, and k [m^2] is the permeability of soil.

According to the method of the radon risk assessment of the building site, the values of radon potential can range between RP < 10 (for low risk); 10 < RP < 35 (for medium risk) and RP > 35 (for high risk) (Neznal et al., 2004).

Radon in indoor air

The indoor measurements of the present survey were performed with the help of nuclear track detectors provided by Radosys Ltd. Hungary, which uses CR-39 chips for passive monitoring of radon in indoor air. Each device consists of a cylindrical plastic vial provided with an appropriate lid and a 1 cm^2 CR-39 chip. The radon present in indoor air enters the vial through the space created between the lid and the vial body. Once inside, the alpha particles emitted during the radon decay hit the CR-39 chip leaving tracks. After 3-month exposure, all detectors are returned to the lab and etched in a 6.25 M solution of NaOH and analysed using a Radosys microscope. The track density found is used to calculate the radon exposure and the indoor concentration for each location investigated. The measurements protocol has already been described in previous papers (Cucoș et al., 2012).

Radon in water

The water samples were collected by means of 500 ml plastic bottles. The bottles were filled completely and tightly closed to prevent the entry of air into the bottle and radon gas escaping from the bottle. The samples were transported to the laboratory in order to determine the radon concentrations with the minimum delay and were measured at the earliest possible time. The radon in water was measured using a LUK-3A device specially adapted for radon in water measurement. This equipment called LUK-VR consists of a 500 ml scrubber in which a known quantity of water (300 ml) is introduced. Before measuring, the water was tempered to room temperature.

RESULTS AND DISCUSSIONS

Radon in soil and permeability measurements

The concentration of radon at six points, respectively the permeability of the soil were determined around the house from Avram Iancu (N: 46,22823 and E: 22,47859) (Table 1).

Table 1. *Radon concentration in soil and soil permeability in the house located in Avram Iancu*

Nr.	Radon concentration (kBq/m^3)	Soil permeability k(m^2)
1	11,91±0,63	2,10E-12
2	16,6±0,8	3.8E-11
3	23,06±1,1	4.5E-11
4	22.06±1,08	4,30E-11
5	24,99±1.15	2,90E-11
6	14,06±0.69	4,60E-12

For the Câmpeni house (N: 46,22150 and E: 23,04834) the determinations for radon concentration and soil permeability were performed in five points (**Error! Not a valid bookmark self-reference.**).

Soil permeability was determined using the Darcy equation, where F = 0.149.

The results of applying the above mentioned equation indicated that there is an average risk of radon emission with a value of 34 for the house of Avram Iancu and a value of 27 for the house in Câmpeni (RP <10 low risk, 10 <RP <35 medium risk, RP> 35 high risk) (Neznal et al., 2004).

Table 2. *Radon concentration in soil and soil permeability in the house located in Câmpeni*

Nr.	Radon concentration (kBq/m^3)	Soil permeability k(m^2)
1	14.02 ± 0.67	4,10E-11
2	2.126 ± 0.09	4.8E-11
3	11,95 ± 0.57	4.5E-11
4	13,71 ± 0.72	4,30E-11
5	1,28 ± 0.06	4,80E-11

Radon in air

Three detectors were placed in each house in the main living quarters: bedroom, kitchen and living room. The results are present in Table 3.

An average radon concentration of 165.6 Bq/m^3 was obtained in the house from Avram Iancu, and an average radon concentration of 154 Bq/m^3 was determined in the house from Câmpeni.

Table 3. *Radon concentration in indoor air in houses located in Avram Iancu and Câmpeni*

Location	Type of room	Radon concentration (Bq/m^3)
Avram Iancu	living room	200
	bedroom	150
	kitchen	147
Cîmpeni	living room	198
	bedroom	165
	kitchen	101

Radon concentration in water

Five water samples were measured from Avram Iancu to determine the dose on people who use it for different purposes. The concentration values of radon in drinking water varies between 7.8 Bq/l and 13.8 Bq/l with an average value of 9.9 Bq/l. Six water samples from Câmpeni were analysed. The results indicated that radon concentration in drinking water varies between 6.9 Bq/l and 10.5 Bq/l with an average value of 8.6 Bq/l. The results are presented in Table 4. The sources of these waters are captured springs or distribution networks.

Table 4. *Radon concentration in water samples from Avram Iancu and Câmpeni*

Location	Source	Radon concentration (Bq/l)
Avram Iancu	spring	8,2
	spring	7,8
	captured springs	10,2
	captured springs	9,8
	spring	13,8
Câmpeni	spring	7,8
	distribution networks	6,9
	captured spring	7,2
	captured springs	9,8
	captured spring	9,4
	captured spring	10,5

Effective doses

The annual effective doses for ingestion and inhalation were estimated according to the parameters introduced by United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR, 2000). The doses obtained due to the indoor radon concentration in both study areas, Câmpeni and Avram Iancu, are the same: 0.95 mSv/year. These values are below the annual limit of the natural dose, which is 2.4 mSv/year but close to 1 mSv/year, which corresponds to the dose that the population receives for one year from natural radon.

The dose due to the intake of radon obtained in Avram Iancu is 0.035 mSv/year and 0.029 mSv/year respectively in Câmpeni. Contribution of the radon to the indoor air in Avram Iancu is 1 Bq/m^3 and 0.82 Bq/m^3 in Câmpeni. These values are insignificant to the contribution of the natural dose of radon: 0.0023 mSv/year for Avram Iancu, 0.0019 mSv/year for Câmpeni.

CONCLUSION

The results of this study clearly indicate that radon concentration in different environmental samples (air, soil, water) from Apuseni Mountain are mostly low and below the proposed reference level of the EU Commission Recommendation (EC, 2001).

Since there are no data on the hydrogeology of the area, the correlation between the geological environment and radon concentrations can only be estimated. Therefore, considering the two types of sedimentary rocks predominant in the geology of the two areas: clastic rocks and carbonate rocks there is the possibility to be a connection between underground waters from clastic and carbonate formations and higher radon concentrations in comparison to underground waters from karstic formations. Moreover, there can be assumed that areas with alternation of clay and sandstone could represent a more important source of radon in soil than limestone of Upper Cretaceous age. This assumption is documented by the lithological heterogeneity of clastic material with different radon potential versus limestone with a lower potential.

Although the highest radon concentrations were expected to be identified in Avram Iancu monitored area, considering its proximity to uranium mineralization, this was not the case, fact suggesting that geology is not the only factor influencing indoor radon concentrations. In Câmpeni, an area with no indication of geology suggesting the presence of radioactive rocks, radon concentrations are most similar to the ones identified in Avram Iancu area.

The risk of radon from the soil calculated from soil radon concentration and soil permeability has a value of 34 for the house in Avram Iancu and 27 for the house in Câmpeni. The results of radon risk indicate that these homes are in areas with medium risk (Neznal et al., 2004). The exhalation of radon from the soil in the studied areas does not add an additional contribution to the natural irradiation of the population.

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STRUCTURAL INVESTIGATION OF SOME NATIVE BIODEGRADABLE PACKAGING MATERIALS

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ABSTRACT. The IR, Raman and NMR methods are used to investigate the structural effects of water and glycerol (plasticizers) on biodegradable packaging materials proceeding from native corn starch. The IR and Raman methods not give a clear response on the amorphous/crystalline content in the investigated starch samples because the origin of vibrational bands is in the same atomic groups of the major starch components (amylose, amylopectin). The nuclear magnetic relaxation data show that the amorphous/crystalline ratio depends not only by the amylose/amylopectin content but also of the mobility and the place of theirs polymer chain segments. The shapes of ^{13}C CP/MAS NMR spectra show clearly the presence of A, B, V-types crystalline structures and also amorphous phase which prevails with the increasing of plasticizers content and also in the extruded starch samples. The composition having starch/glycerol/water 68/17/15 mass % ratio was found to have a dominant amorphous character and very similar features with a commercial specimen (USA) used for the package. It was also found that this best package is extremely degraded after just one day under water absorption.

Key words: *starch, plasticizers, IR, Raman, NMR*

INTRODUCTION

The native starch is used as the main component of biodegradable packaging materials and also in the textile, pharmacological and the food industry (Almeida et al., 2010; Liu et al., 2009; Luckachan and Pillai, 2011). It has a granular structure with an internal architecture characterized by concentric rings involving semi-crystalline shell (thickness 120-400 nm) separated by essentially amorphous regions (Wang et al., 2009). Chemically, the starch contains two glucose polymers amylose and amylopectin (Liu et al., 2006).

Amylose is essentially a linear structure of α -1,4 linked glucose units, and amylopectin is a highly branched structure of short α -1,4 chains linked by α -1,6 bonds (Liu et al., 2009). Amylose and the branching points of amylopectin form the amorphous regions in the starch granules. Amylopectin is the main crystalline component in granular starch (Soesta and Vliegenthartb, 1997). The physical-chemical properties of starch as viscosity, gelation power, adhesion etc., are strongly influenced by the amylose/amylopectin ratio (Almeida et al., 2010; Cereda et al., 2002).

The plasticizers molecule (water, glycerol) and other proceedings as annealing extrusion or enzymatic digestion can destabilize the crystalline regions and increase the amorphous domains (Brümme et al., 2002; Lopez-Rubio et al., 2008; Warren et al., 2016).

There are four types of crystalline structures in starch materials. From these the A-type is due to the junction of amylopectin short branches to backbone chain (lowest mobility) close to each other and appears in corn, wheat or rice cereals. In fruit and tuber starches prevails the B-type structure realized by amylopectin polymer chain segments located away from junctions in core branches region (more mobile). The V-type structure is formed by inclusion complexes between amylose and water, glycerol, alcohols molecules (plasticizers) stabilized by hydrogen bonds. There is also a C-type crystalline structure in leguminous plant, which is in fact a mixture of A and B-type structures (Cioica et al., 2013). Amorphous phase is due to mobile laterale branches of amylopectin and free chains of amylose.

The native starch materials used in the packaging process must to have a high content of amorphous phase and biodegradability at natural agents (Luckachan and Pillai, 2011). Besides the presence of plasticizers generally is also used the extrusion process what disrupts and transforms the semi-crystalline structure of starch granules in a homogeneous amorphous material with increased biodegradability (Mościcki et al., 2012; Nabar, 2006). The effect of the nature and content of the plasticizers (water, glycerol) on the native corn starch properties (crystalline/amorphous) and also on the degradation process after absorption of distilled water were investigated by vibrational (IR, Raman) and nuclear magnetic resonance (NMR relaxation, ^{13}C CP/MAS NMR) spectroscopies.

EXPERIMENTAL

The native corn starch used in this study was obtained from SC Amylon Sibiu, Romania, having water content of 10.76 %, a density of 0.561 g/cm^3 and an amylose content of 21%. The glycerol used was purchased from SC Nordic Invest SRL Cluj-Napoca and had a concentration of 99.5% and a density of 1.262 g/cm^3. The water used was from the water supply system.

Two sets of samples with different starch / glycerol / water [%] ratios were prepared. First set of samples have the ratio starch / glycerol (= 4) constant and the added water content increased from 0 up to 15% (0; 2.5; 5; 7.5; 10; 12.5; 15). Samples from the second set have constant the ratio starch / water (= 5.7) and the glycerol content increases from 0 up to 16.5% (0; 2.5; 6; 9.5; 13; 16.5).

FT-IR/ATR spectra were recorded at room temperature on a conventional Equinox 55 (Bruker, Germany) spectrometer equipped with a DTGC detector, coupled with an ATR sampling device (Miracle, Pike Techn.). The resolution was of 2 cm^{-1}. The ATR crystal is of ZnSe and we made 40 acquisition for obtaining IR spectra.

FT-Raman spectra were recorded with a resolution of 4 cm^{-}1 in a backscattering geometry with a Bruker FRA 106/S Raman accessory equipped with a nitrogen cooled Ge detector. The 1064nm Nd:YAG laser was used as excitation source, the laser power measured at the sample position was 300mW.

The ^{1}H NMR relaxation measurements were obtained using the Bruker Minispec spectrometer with the 10 mm probe-head working at 19.688 MHz Larmor frequency. In all measurements the temperature was set at 35 ^{o}C. The CPMG (Car – Purcell – Meiboon – Gill) decays and saturation recovery curves were analyzed using the UPIN (Uniform – Penalty Inversion) algorithm, which perform a Laplace inversion of the measured data (Borgia et al., 1998). In this way the T_1 (spin-lattice) and T_2 (spin-spin) relaxation times distributions as function of samples composition were analyzed.

The ^{13}C solid state cross-polarization magic-angle-spinning (CP/MAS) NMR spectra were recorded on a Bruker Avance III wide-bore spectrometer operating at 125 MHz Larmor frequency for ^{13}C, using a 4 mm double resonance probe head. Standard ^{13}C CP/MAS experiments were analyzed at room temperature, using a spinning frequency of 14 kHz and a ^{1}H 90° pulse of 2.3 μs. The ^{13}C CP/MAS spectra were calibrated using the $^{13}CH_3$ line in TMS through an indirect procedure which uses the carboxyl NMR line in α-glycine.

RESULTS AND DISCUSSION

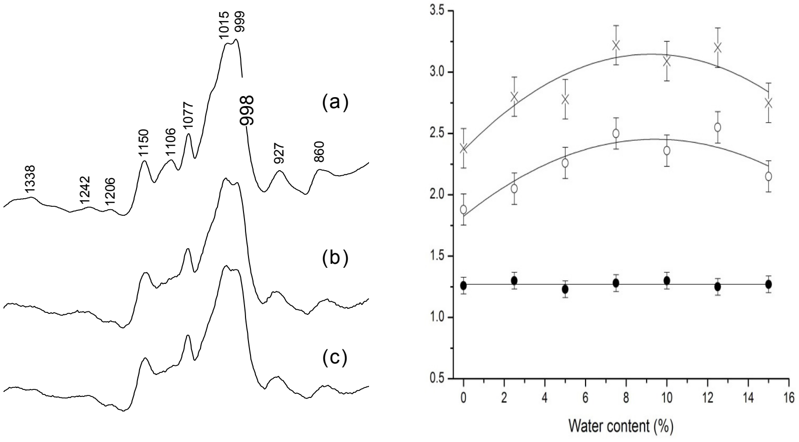
Vibrational spectra

The characteristic IR spectra of starch samples with different amounts of plasticizer agents (water, glycerol) are situated in the 2900 cm^{-1}, 1340 cm^{-1} and 1000 cm^{-1} regions. These spectra contain also two bands at 3300 cm^{-1} and 1610 cm^{-1} due to the water stretching and bending vibrations (Morales et al., 2012; Iizuka and Aishima, 1999).

The absorptions situated at 2930 cm^{-1} and 2850 cm^{-1} are assigned to symmetric and asymmetric stretching vibrations of CH_2 groups [16] and those from 1350 cm^{-1} region to bending modes of O-C-H, C-C-H and C-O-H angles of amylose and amylopectin formations (Bellon–Maurel et al., 1995).

The peaks from the 1150 – 900 cm^{-1} region are due to C-C and C-O stretching vibrations (Wilson and Belton, 1988).

According to Capron et al., 2007, the intense absorption from 998 cm^{-1} may be assigned to crystalline domains whereas the band at 1015 cm^{-1} reveals the amorphous contribution of plasticizers in starch samples (figure 1A).



A B

Fig. 1. *A. - The FT-IR spectra (in cm^{-1}) of starch / glycerol / water = 68/17/15 mass% sample before (a) and after extrusion (b) and of commercial specimen – USA(c). B - The dependence of 998 / 2929(x), 1015/2929(o) and 998/1015(•) ratios band intensities versus water content*

The evolution of the 998 / 2929 and 1015 / 2929 band intensity ratios versus water content (0 – 15 %) at a constant starch: glycerol ratio of 4 : 1 suggest a similar behavior (a parallelism) between increase and decrease of the crystalline / amorphous domains in the investigated starch samples with various plasticizers contents (figure 1B).

The constancy of 998 / 1015 ratio with the increase of water content suggests an absence of structural order at the FTIR observation range. A similar situation is also mentioned for the 1000 / 1022 cm^{-1} ratio in the case of extruded starch and granular starch with water content under 20% (Capron et al., 2007).

The band from 1015 cm^{-1} becomes more intense than that situated at 998 cm^{-1} in the extruded sample (figure 1A, b, c) being similar with a commercial specimen (USA). The extrusion process made with a co-rotating intermeshing twin-screw extruder ZK 25 (Collin, Germany), disrupts and transforms the semi-crystalline structure of starch granules in a homogeneous amorphous material which increase their biodegradability.

Raman spectra contain the two intense bands at ~ 2900 cm^{-1} attributed to the symmetrical and antisymmetrical CH_2 stretching vibrations (Almeida et al., 2010; Morales et al., 2012). Their intensity can be related to the amount of amylose and amylopectin content in the starch samples (Kizil et al., 2002).

The 1461 cm^{-1} band corresponds to the superposition of CH, CH_2 and C-O-H bending vibrations (Benzerdjeb et al., 2007) and those from 1380 cm^{-1} and 1340 cm^{-1} are due to C-O-H deformation modes and to the superposition of C-O stretching and C-O-H deformations, respectively (Almeida et al., 2010; Gussem et al., 2005).

The 1200 cm^{-1} - 1000 cm^{-1} region is characteristic of the C-O and C-C stretching and C-O-H deformation modes (Nikonenko et al., 2005; Yang and Zhang, 2009).

The bands observed at 940 cm^{-1} and 860 cm^{-1} are due to the superposition of bending C-O-C, C-O-H and stretching C-O vibrations from amylose α-1,4 glycosidic linkage (Almeida et al., 2010) and also to the superposition of C-C-H and C-O-C deformations, respectively (Gussem et al., 2005).

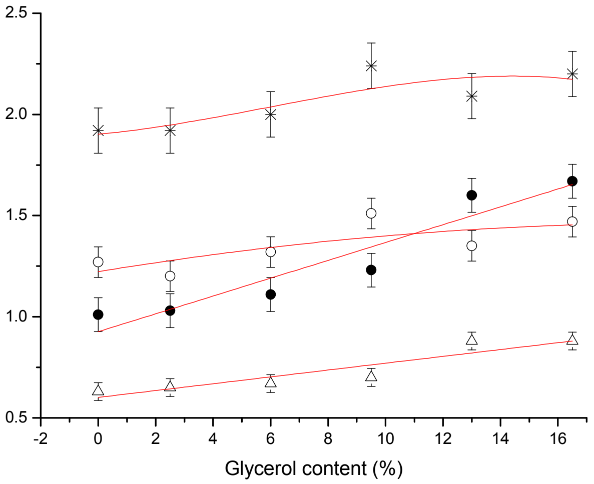


Fig. 2. *The dependence of 2900 / 1123 (∗), 1460 / 1340(•), 2900/477 (o) and 869 / 940 (Δ) ratios band intensities versus glycerol content and starch / water ratio constant (5.7). The errors bars are under 5% error limits*

An other intense 477 cm^{-1} Raman band is due to the superposition of bending C-C-C and twisting C-O vibrations and is used as a marker to identify the presence of starch in different samples.

The glycerol (OH · CH_2 · CH(OH) · CH_2 · OH) stretching ν_s, ν_{as} – CH_2 vibrations, the in plane δ -CH_2 deformations and CC stretching vibrations contribute to the following starch bands: 2900 cm^{-1}, 1461 cm^{-1} and 860 cm^{-1}, respectively.

An easy increase of the 2900/1123 (*), 2900/477 (o) and 868/940 (Δ) ratios band intensities may be observed for the samples, with starch / water ratio of (5.7) and the added glycerol increasing up to 16.5% (figure 2). These suggest that the amylose / amylopectin ratio remains practically unchanged and plasticizing – antiplasticizing effect depends on the levels of realized hydrogen bondings which lead to decrease - increase the rigidity of starch components.

The more pronounced increase of the 1460/1340 (•) band ratio is due to the glycerol contribution at 1461 cm^{-1} band by the in plane bending CH_2 vibrations from the inclusion complex realized between amylose and glycerol molecules by hydrogen bonds (V – type structure).

NMR data

The nuclear magnetic relaxation method (Cioica et al., 2013) offer information's on the structure of monomer units by direct spin–spin interactions (T_2) and also on the supramolecular organization by spin diffusion, spin–lattice relaxation (T_1).

A number of three peaks, two intense at T_2 ~ 0.2 ms and T_2 ~ 1 ms and also a small peak at T_2 ~20 ms are observed for pure starch and for a mixture of starch with water (figure 3).

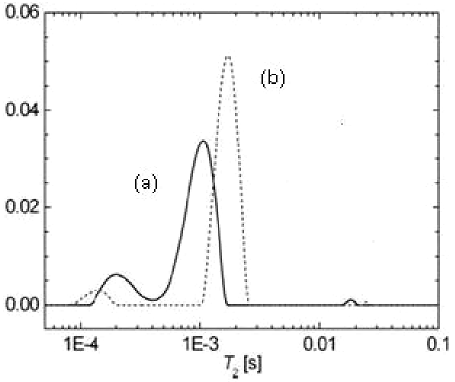


Fig. 3. *The spin-spin relaxation times T_2 distribution of starch (a) and 85% starch + 15% water (b)*

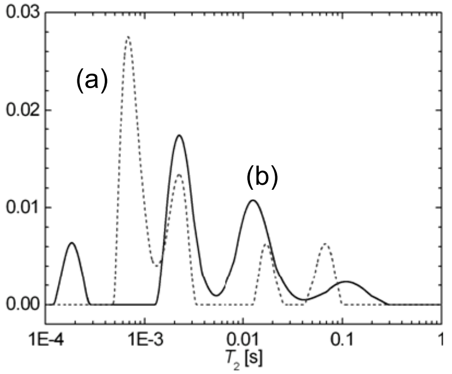


Fig. 4. *The spin-spin relaxation times T_2 distribution of 80% starch + 20% glycerol (a) and 68% starch +17% glycerol +15 % water (b)*

The peak from T_2 ~ 0.2 ms may be associated with starch polymer chain segments with the lowest mobility (A – type structure) due to the junction of one end of amylopectin branches to backbone chain. The second component with T_2 ~ 1ms may be associated with more mobile amylose and/or amylopectin polymer chain segments located away from junctions in core branches region (B – type centers). The minor T_2 component located at ~ 20 ms presents a dynamic liquid-like behavior and can be associated with the mobile lateral branches of the amylopectin microstructure or free chains of amylose microstructure (amorphous). The small integral area of this peak suggests that the percentage of lateral branches is small, leading to the idea that the starch molecules are closely packed (crystalline).

By adding 15 % of water one can observe a displacement of semi-mobile (T_2 ~ 1ms) and mobile (T_2 ~ 20ms) peaks to higher T_2 values and a decrease of the rigid component (T_2 ~ 0.2 ms). Thus the additional water content lead to a larger mobility of amylopectin polymer chain segments in the core packed branches.

The mixture between starch with glycerol (Fig.4a) leads to a distribution characterized by four peaks. The significant dynamic components remain in the semi-mobile region (peaks centered at T_2 ~0.6 ms and 2.5 ms) and the other two peaks situated at larger T_2 values of ~20 ms and ~70 ms suggest that glycerol increases the number of lateral branches and may create mobile free ends in amylose and amylopectin polymer chain segments finally leading to an increase of mobility of the starch polymer chains (amorphous).

An increase in intensity of the last three major components can be observed in the T_2 distribution for the mixture of starch with glycerol and water (Fig.4b). This can be interpreted as a transformation of amylopectin microstructure where the lateral branches are moved away from the core branches with the creation of more mobile free ends (amorphous). However, it should be noted that the presence of additional water molecules can maintain a rigid dynamic component (crystalline) of the starch polymer chain segments (peak located at ~ 0.2 ms) corresponding to amylopectin segments around junctions.

The ^{13}C CP/MAS NMR spectrum (figure 5a) suggest the presence of both crystalline and amorphous phases in the case of the 68% starch/ 17%glycerol/ 15%water sample as shown also by the NMR relaxation data (figure 4b).

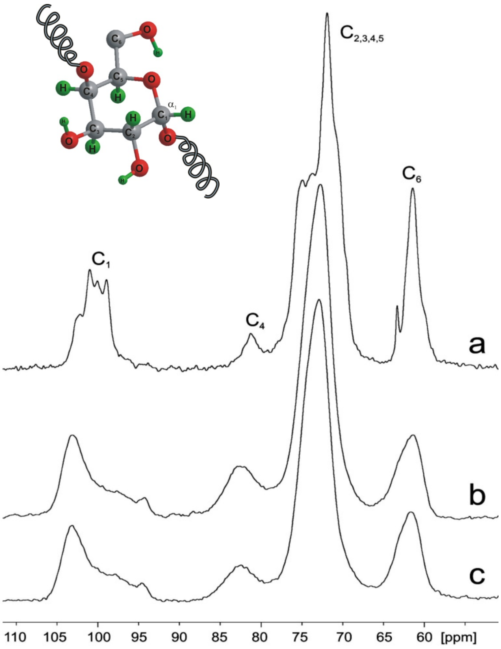


Fig. 5. *The ^{13}C CP/MAS NMR spectra of starch / glycerol / water [mass %] formula with 68/17/15 ratio, a – before and b – after extrusion and c – commercial USA extruded product, recorded at room temperature and 14 kHz spinning speed*

Before extrusion, the A, B and V- crystalline structures are present (figure 5a). In the region of the glucose unit C1 NMR resonance there is an overlap of the *triplet* at δ = 101 ppm (A phase), the *doublet* at δ = 101 ppm (B structure) and a *singlet* at δ = 104 ppm (V type structure).

The strong C 2,3,4,5 *quadruplet* from δ = 73 ppm is characteristic of A – type phase.

The intense C6 absorbtion (δ = 62 ppm) is due to contributions from A, B, and V – types crystalline phases (Wang et al., 2009; Therien and Zhu, 2009). All these absorbtions are situated over the weak and broad NMR resonances at δ = 104 ppm (C1), δ = 83 ppm (C4) and δ = 61 ppm (C6) characteristic of the amorphous phase as in the extruded samples (b, c).

The sharp ^{13}C line at δ = 64 ppm belongs to inclusion glycerol – amylose complex stabilized by hydrogen bonds.

Degradation process

Environmental degradation of biopolymers may be defined as the scission of chemical bonds in the polymer backbone by the attack of water to form oligomers and finally monomers (Shah et al., 2008). The degradation of starch – based packaging required unstable and hydrolysable linkages where chemical, biological or photochemical reactions can take place with the disintegration into their monomers (Wollerdorfer and Bader, 1998).

By following the absorbed water process during five days we found that the product with the high starch content (78/19.5/2.5 starch/glycerol/water – (a)) is most resistant and start to be degradated after only five days (figure 6a).

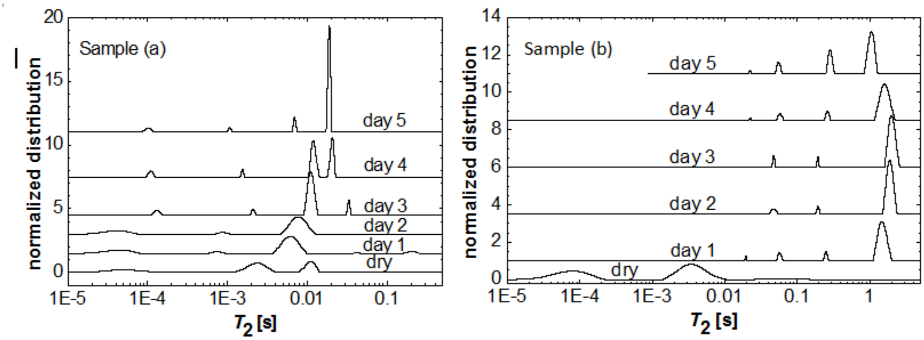


Fig. 6. The normalized T_2 relaxation times distributions of packages samples (a) and (b) for 5 days water absorption compared with dry sample

A semi-mobile phase (T_2 ~ 2.5 ms and ~11 ms) and also a rigid region (T_2 ~ 50 μs) due to the junctions of lateral branches with the amylopectin polymer backbone can be observed for dry sample (a). After one day the two mobile peaks collapses to a unique peak located at T_2 ~ 6.3 ms (figure 6).

Dramatically changes can be observed starting with day 3 when that the T_2 peaks becomes more narrow indicating a reduced distribution compared dray sample or with not so degraded sample (first two days). Their shifts to larger T_2 values compared with the values measured in day 2, suggest the presence of most mobile components.

The product with lower starch content (68/17/15 starch/glycerol/water – (b)) is degraded after one day becoming a colloidal aspect. The dry sample (b) is characterized by two relative rigid components ($T_2 \leq 5$ ms). The amorphous phases prevail in this sample ($T_2 > 10$ ms) after one day (figure 6).

With day 4 a precipitation validated by the decrease in intensity and shifted at lower values of the main peak (more mobile $T_2 \sim 1$s) can be observed for sample (b). A similar behavior was also observed for commercial USA specimen.

CONCLUSION

The IR and Raman methods not give a clear response on the amorphous or crystalline content in starch samples because the vibrational bands have the origin in the same atomic groups of the major starch components.

The relaxation NMR spectroscopy shows that the amorphous / crystalline ratio depends on amylose / amylopectin mobility and also by the place of their polymer chain segments. The distributions of spin – spin (T2) and spin – latice (T1) relaxation times values and theirs shift toward higher values show that the increasing of water and glycerol content in the starch package samples (68/17/15) lead to the more mobile amylose and amylopectin polymer chain segments and the prevalence of amorphous phase.

^{13}C CP/MAS NMR spectra show also that in the extruded samples the amorphous phase becomes dominant.

The most amorphous package with starch/glycerol/water of 68/17/15 mass% ratio is extremely degraded after just one day by the water absorption, forming a colloid substance. The package with a large content of starch (78/19.5/2.5) is most resistant, starting to be decomposed after five days.

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INDOOR RADON RELATED WITH THE GEOLOGY IN ROMANIAN URBAN AGGLOMERATIONS (CLUJ-NAPOCA)

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ABSTRACT. Radon is a natural radioactive gas that occurs due to the radioactive decay of radium (^{226}Ra) present in rocks which, in turn, cames from the radioactive decay of uranium (^{238}U), a primordial natural element. Along with factors such as porosity, permeability and humidity of the rocks and soils, pressure and temperature, geology setting plays one of the most important roles in the release of radon into the environment. Depending on the mineralogical compositions and characteristics of the bedrock from a certain area, a higher or lower concentration of radioactive minerals can be found in the rocks, which will directly influence the level of radon in the atmosphere, implicitly the concentration of radon measured in houses. In this study, a six months concentration of radon (^{222}Rn) was assessed in 256houses from Cluj-Napoca area using CR-39 nuclear track detectors. Correlations between the indoor radon levels and the geological setting was further analyzed. The aim is to better understand the influence of geology on the concentration of radon levels in homes, in order to further identify other risk areas in terms of exposure to radon. Further investigation is needed on other factors influencing the accumulation of radon in high concentrations indoor, such as ventilation, occupation patterns or constructive and architectural features for typical houses. Therefore, the results of this work are considered to be important for indoor radon management in Romania.

Key words: *indoor radon, radon exposure, indoor air quality*

INTRODUCTION

Radon is a natural radioactive gas, considered to be the main contributor to the total dosage received by population from natural background radiation. Due to its radioactivity and short lived radioactive disintegration products, it is also considered to be a health hazard. Far more, it is largely recognized that long term exposure to radon in homes and workplaces is the main leading cause of lung cancer, second to smoking (Darby et al., 2005; Field et al., 2006, Council Directive 2013/59 /Euratom; WHO 2009). Geology is considered, by far, the most important factor controlling the source and distribution of radon. This, due to the fact that most of natural uranium (^{238}U) where the radon (^{222}Rn) comes from, is encapsulated in rocks in the form of minerals. Nevertheless, several other natural and anthropogenic factors such as weather conditions, building materials, the degree of containment in the areas where individuals are exposed, outside air, tap water and even city gas, the architecture, ventilation and the environmental parameters of the building and the soil (temperature, pressure, relative humidity) and occupation patterns can influence the indoor radon levels (Darby et al., 2005; Field et al., 2006, Council Directive 2013/59 /Euratom; WHO 2009; www.irart.ro; www.smartradon.ro; Cosma and Jurcuţ, 1996; Cosma et al., 2013; Cucoş et al., 2015; Cucoş et al., 2017).

Reducing exposure to radon in buildings is a key priority of public health protection against radiation. Directive 2013/59 / Euratom is demanding an increased attention to residential radon by implementing rules in each European country, beginning in 2018, and serious approach to monitoring and mitigating actions.

Since September 2016 we have started a research pilot project entitled SMART-RAD-EN, funded by the Competitiveness Operational Programme 2014-2020 of Romania, to be implemented up to the year 2020. The project aims to develop and implement energy efficient solutions for controlling and reducing exposure to radon in residential buildings located in the main urban agglomerations of Romania (Bucureşti, Cluj-Napoca, Timişoara, Iaşi and Sibiu).

The present paper reports the results for the first measurement campaign of indoor radon concentration during six months, in 256 houses from Cluj-Napoca area, by using CR-39 nuclear track detectors. Some basic correlations between the indoor radon levels and the geological setting were analyzed. The aim of this study is to better understand the influence of the geology on the concentration of radon levels in homes.

MATERIALS AND METHODS

Geological data

Various detailed studies were focused on the geology of the Cluj-Napoca city area (e.g. Răileanu and Saulea, 1956; Maxim et al., 1960; Mészáros, 1960; Mészáros and Clichici, 1976; Popescu et al., 1978 etc.). The region which the city belongs to comprises a large diversity of rocks and lithostratigraphic units involving: magmatic, metamorphic and sedimentary rocks (Fig. 1).The metamorphicsole is the oldest structure in the area (Precambrian). It is mostly formed in the basal part by paragneiss, quartz and mica schist, with quartzite, amphibolite and crystalline limestone interleaving. The upper levels bear mica schist with black and white mica. The first sedimentary rocks overlying the sole are Late Cretaceous reworks in the basal section crystalline schist, than bear sandstones, clay, limestone and polygenic conglomerates. All these rocks are overlain by a transgressive Cenozoic sedimentary succession (Paleogene, Neogene and Quaternary).Andesitic and dacitic dykes were reported from the western part of the studied area (Mészáros and Clichici, 1976).

The Paleogene starts with lowermost Paleocene red beds, probably including the K/T boundary, if considering the situation from the Jibou Formation type section area (Codrea and Godefroit, 2008). Classical stratigraphic charts of the region are in Codrea et al., 2010 (and references therein). In this regard, the basal continental Paleogene formation is overlain by marine rocks, documenting a Lutetian transgression, the marine realm continuing until Priabonian. Gypsum beds are largely exposed. They are followed by various marl, limestone and sandstone deposits (Raileanu & Saulea, 1956; Mészáros and Moisescu, 1991; Popescu et al., 1978). In Late Priabonian, terrestrial environments occurred again, with red beds (Valea Nadășului Formation). Various marls, bioclastic limestone's, clays, coaly schists, and shallow water limy sedimentary rocks accumulated in the latest Eocene and Lower Oligocene.

The Oligocene of this region is nothing but alternating marine and continental formations, with various rocks, either clastic, or carbonatic (Codrea et al., 2010, and references therein).

Glauconitic and mica rich clays and tuffs occur in Early Miocene (Aquitanian-Burdigalian). In Middle Miocene (Badenian-Sarmatian), gypsum, salt and marls are the most common rock, but the clastic ones occur too (Filipescu, 2001). In Quaternary, the Someș and Nadașului river terraces were formed. Nowadays, alluvial deposits (sand-sand gravels) continue to accumulate.

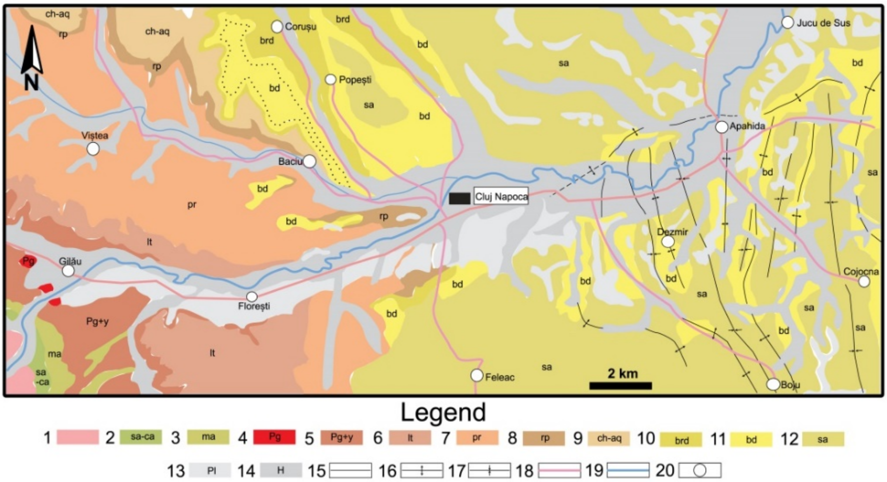

Fig. 1. *Geological map of Cluj-Napoca Area (modified after IGR map, L-34-XII, 1:200 000) 1: Proterozoic, 2: Cretaceous (Santonian-Campanian), 3: Cretaceous (Maastrichtian), 4: Paleogene andesitic dykes, 5: Paleogene (Paleocene-Ypresian), 6: Eocene (Lutetian), 7: Eocene (Priabonian), 8: Oligocene (Rupelian), 9: Oligocene-Miocene (Chattian-Aquitanian), 10: Miocene (Burdigalian), 11: Miocene (Badenian), 12: Miocene (Sarmatian), 13: Quaternary (Pleistocene), 14: Quaternary (Holocene), 15: faults, 16: Syncline axis, 17: Anticline axis, 18: Roads, 19: Rivers, 20: Locality*

Indoor radon

Passive indoor radon measurements were performed by using CR-39 nuclear track detectors exposed for 6 months. Subsequently, the detectors were safely transported (storage in another room could affect the measurement accuracy) to the Radon Laboratory for processing. Processing, analysis and comprehensive evaluation of the measurement results were achieved in cooperation with the manufacturer, according to the specific protocol and calibration factors. After exposure, the developing and automatic reading protocol was applied by using the RadoSys-2000 equipment (Elektronika, Budapest, Hungary), under optimum conditions. The concentration of radon was determined by counting the traces of alpha particles resulting from the decay of radon on a given area. Individual errors for radon measurements by this method are less than 10%. The accuracy of this passive method of detection is being periodically verified by successful participation in international intercomparison campaigns (Cucoş et al., 2012; Cosma et al., 2013; Cosma et al., 2015).

Qualitative assessment of indoor air quality conditions, health and comfort of residents was done through questionnaires, applied to each resident of the investigated homes, according to the model of RADPAR (Radon Prevention and Remediation). Through the questions was determine the details of how the building is used, occupation program, occupants opinions on air quality and functioning of the systems in the house, periods of overheat or winter comfort, in order to analyse possible correlations between the level of radon and other household air pollutants and specific characteristics of energy-efficient houses. The questionnaire also requests general information about residents health and behaviour, smoking status, location and building structure, facilities and materials used, as well as information about the energy performance of buildings: the type of exterior wall insulation, exterior facade status, number of levels, heating sources (boiler, stove), windows type (double wooden windows, double glazing, triple glazing) existing ventilation systems, winter and summer temperature, air quality, draughts, building's energy consumption, etc.

RESULTS AND DISCUSSION

Summary statistic of radon concentration measurements in air of residential premises from Cluj-Napoca are presented in Table 1.

The data distribution type, within the investigated cities, is a log-normal distribution, aspect confirmed by applying the D'Agostino-Pearson statistical test on the log-transformed data ($p > 0.05$).

Table 1. *Descriptive statistic for indoor radon concentration in houses from Cluj-Napoca area under SMART_RAD_EN project*

N_{house}	C_{Rnmin} (Bq/m^3)	C_{Rnmax} (Bq/m^3)	A.M. (Bq/m^3)	S.D. (Bq/m^3)	G.M. (Bq/m^3)	C.V. (%)	No. > 300Bq/m^3
256	5 (21)	720	139	133	95	96	43

From the 256 houses selected for the present study in the metropolitan area of Cluj-Napoca, 43 presented concentrations higher than 300 Bq/m^3. Given that the computed averages refer only to a period of six months of monitoring - and are not annual concentrations - it is necessary to apply a seasonal correction factor, in order to evaluate the annual values. Thus, by applying the seasonal correction factor, from the 256 monitored houses, a total of 52 have annual mean for indoor radon concentration superior to the threshold value.

The distribution of indoor radon results for the city of Cluj-Napoca within Campaign I indicate that 17% of the investigated residential dwellings present values higher than the European reference level of 300 Bq/m^3 for residential radon (Tollefsen et al., 2014), while 20% of the investigated houses register radon levels higher than 250 Bq/m^3 (figure 2).

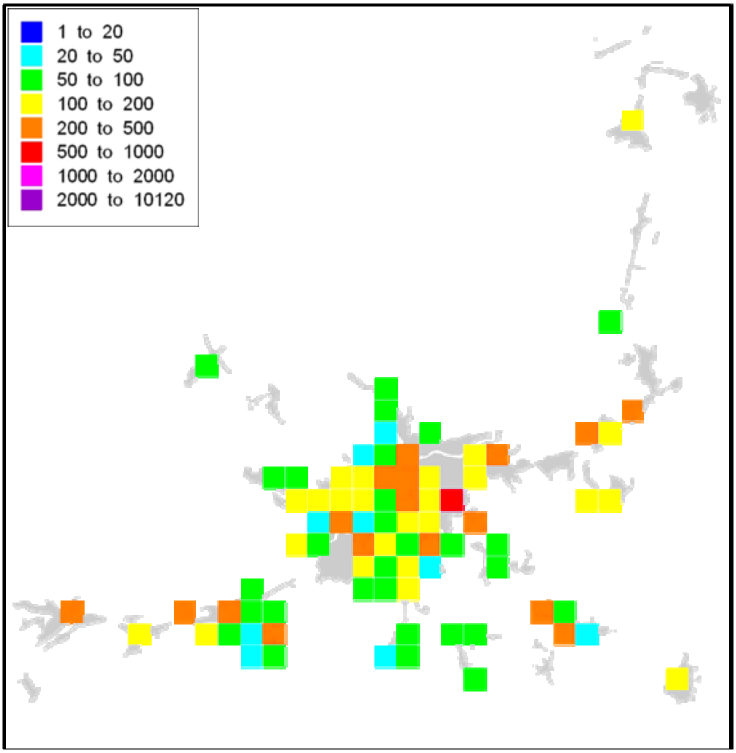

Fig. 2. *The indoor radon map for houses of Cluj-Napoca under the SMART_RAD_EN project*

The average for all measurements performed for the concentration of indoor radon within accommodations monitored in this project, is 138 Bq/m^3, higher than the values reported for other countries, and higher than the value of 98 Bq/m^3, reported as average exposure to indoor radon for Europe (Tollefsen et al., 2014), and comparable with the values registered for the Czech Republic and Estonia (140-160 Bq/m^3), which can be explained through the existing resemblances in relief and geology.

The rock types that are most likely to cause elevated indoor radon levels in some countries, are considered to have uranium concentrations greater than 2ppm (Gundersen et al., 1992). In this regard, some examples can be given by some magmatic (granites, riolites, andesites and basalts), metamorphic (gneiss and some schists) and sedimentary (argillaceous schists and clays) rocks. For Romania, the most radioactive sedimentary rocks are considered to be clays (with an average uranium concentration of 3.3 ppm), sandstones (with an average uranium concentration of 3 ppm) and argillaceous schists (with an average uranium concentration of 3 ppm) (Cosma et Jurcuț, 1996; Stoici et Tătaru, 1988). However, lower or higher uranium values can be measured in all types of rocks, regardless of their origin.

For this assessment, the rock types that were more likely to cause the high levels of radon concentrations, measured in houses, are considered to be sedimentary rocks, which include clays and sandstone deposits, largely found into the Paleogene and Neogene bedrock assemblage. Although these sedimentary deposits are not uniformly distributed, decreasing in age from West to the East, clays and sandstones are widely spread in the whole geological complex.

Considering the geological context and the fact that the indoor radon concentration values are not evenly distributed in the houses, by not showing a pattern (figure 2), we can assume that even though the geological factors are responsible for the radon emissions, they are not the only ones to influence the indoor concentrations. Other factors that influence the concentration of indoor radon are represented by architectural details of houses.

CONCLUSIONS

The present paper report the results for the first measurement campaign of indoor radon concentration during six months in 256 houses from Cluj-Napoca area by using CR-39 nuclear track detectors. The preliminary indoor radon map for Cluj-Napoca area was plotted, taking into account the geological context. The aim of this pilot study is to better understand the influence of geology on the concentration of radon levels in homes.

The study shows that average indoor radon concentration for the surveyed area is 138 Bq/m^3. The indoor radon results indicate that 17% of the investigated residential dwellings present values higher than the European reference level of 300 Bq/m^3 for residential radon, while 20% of the investigated houses register radon levels higher than 250 Bq/m^3.

Even though the principal factor for high radon concentrations appear to be the geological bedding by the presence of rock type known to have relatively high radioactive contents (clays and sandstones), it is clear that there are other aspects to be considered. Those aspects can include some geological factors influenced by ground waters, climate change, permeability of soils and rocks, along with antropogenic factors.

Further investigation is needed on other factors influencing the accumulation of radon in high concentrations indoor, such as ventilation, occupation patterns or constructive and architectural features for typical houses, together with soil radon measurements.

After carrying out the project activities, an inventory of indoor air pollution in conjunction with energy consumption will be completed for 1,000 houses from Bucharest, Cluj-Napoca, Iasi, Sibiu and Timisoara, and also integrated into a geographic information system and processed for use in the air quality modelling.

Acknowledgements

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APPEARANCE OF WATER MICROPOLLUTANTS IN WATER AS EFFECTS OF EXTREME METEOROLOGICAL EVENTS

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ABSTRACT. The objective of the present study is to obtain data on micropollutants sources present in surface and drinking water after extreme meteorological events in Romanian regions. The analyses were performed on water samples collected from potable water sources using GC/MS method after LL extraction. Were detected and discussed anthropogenic compounds from following compound groups: lubricant and plastic additives and hydrocarbons. The compound identification was done based on mass spectra obtained by electron impact ionisation in full scan mode.

Key words: *emerging contaminants, extreme events, lubricant additives, mineral oils*.

INTRODUCTION

Human activity is causing the atmospheric accumulation of greenhouse gases, increasing temperatures, and producing changes in the hydrologic cycle (Louis et al., 2008)

These climatologic changes, contribute to a wide variety of effects, including direct effects on temperature and climatologic instability, such as heatwaves, drought, and increased frequency and severity of extreme precipitation events (Yeomona et al., 2017; WHO 2011; FCM 2004; Alderman et al., 2012).

By studies of the environmental events a real relationship was observed between extreme rainfall and elevated concentration of different organic pollutants. Heavy rainfall events are characterized by high volumes of water, increased flow rates, and, consequently, more significant run-off transportation of suspended solids and possibly chemical and biological substances. The quality of water resources (surface water and groundwater) can be severely impacted, and the quality of the associated drinking water may also be degraded. Flooding is a seriously contaminant transfer mechanism to river catchments (Bei et al., 2016; Corada-Fernandez et al., 2017; Roig et al., 2011).

Human activity continues to add an increasing variety of organic compounds into the environment or has changed the ratios and amounts of naturally compounds. Both anthropogenic and naturally occurring compounds are found mixed together in recent environmental samples and several of these compounds may be used as tracers to study natural processes affecting the fate and effects of chemical contaminants in water.

The occurrence of pollutants in streams resulting from surface runoff, from agricultural and industrial fields has been documented in several studies (Rasmussen, 2011). Because of the hydrodynamic situation during the meteorological event, sedimentation and resuspension phenomena can be considered negligible (Ciaponi et al., 2002). Furthermore, surface runoff has often been emphasised as important entry routes chemicals to streams having a potential impact on drinking water sources. The quantity of anthropogenic compounds released into environment and their potential adverse effects to environmental and human health represent major challenges in the scientific community. For that reason, developments in instrumentation and methods are increasing towards the study the structure and quantity of the compounds present in environmental matrices. In respect to this, one of priorities is to determine the environmental distribution of organic pollutants in the surface waters.

The objective of the present study is to obtain data on micropollutants sources present in surface and drinking water after extreme meteorological events in Romanian regions. The results of micropollutants detection in a potable water source are presented. The analyses were performed using GC/MS method after LL extraction. The compound identification was done based on mass spectra obtained by Electron Impact Ionisation in full scan mode. The results are discussed in connection to main families of compounds with high potential for entering in the surface water in flood condition (Cavestri, 1997; ATC 2007; AccuStandard, 2013*)*.

EXPERIMENTAL

Study area

Sampling site was a drinking water well from north region of Transylvania (Romania) at few days after a flood caused of a very abundantly rain (60 l/m^2), in the summer of the 2016. The well is very common source of potable water in this region. Climatic conditions are temperate and average annual precipitation is about of 635 mm. Main of the total area is used for agricultural activity. Dominating crop types are cereals followed by grasslands and maize.

Instruments

The compounds concentration were performed by extraction liquid-liquid (LL) using hexane as solvent after acidulation at pH 2 and filtrated (Glass filter of 0.47 um). Analysis was carried out using a gas chromatography – mass spectrometer (Polaris, Thermo-electron Corporation, USA). The chromatographic separation was accomplished by an HP-5MS column (l = 30m, d_i = 0.25 mm) with helium as carrier gas at a flow rate of 1.5 mL/min. The GC oven temperature was programmed from 90 ^{0}C (hold 1 min) to 120 ^{0}C (at 20 ^{0}C/min, then to 300 ^{0}C (hold 10 min) at 4 ^{0}C/min. The injection port temperature was set at 250 ^{0}C. Mass spectrometric analysis was performed by MS operating in electron impact (EI) mode at 70 eV and with the ion source temperature at 250 ^{0}C. The mass spectra were obtained in full scan mode in the range 50-650 Daltons.

RESULTS AND DISCUSSION

The composition of surface and underground waters depends strong of natural factors. The early studies conducted in different countries show that storm water runoff from roadways and also from other areas (car parks, service stations etc.) are highly contaminated and have a negative impact on receivers (Papiri et al., 2008). Characteristic of pollutants transported, varies with runoff volumes, water levels and weather conditions (Pizarro et al., 2007).

The pollutants identified in this study are from family of plastic additives (AccuStandard, 2013) and lubricant additives (ATC, 2007). The compounds separation is shown in the figure 1 and figure 2. The identification of compounds from family of lubricant antioxidants is presented in table 1.

Table 1. *Identification of compound from figure 1*

No	Molecular Weight	Name	Compound family
1	236	3,3-dimethyl-1,1-diphenyl-1-butene	Lubricant additives
2	268	2-t-Butyl-4-methyl-6-(amethylbenzyl)phenol	
3	268	2-t-Butyl-4-(dimethylbenzyl)phenol	
4	324	4,6-Bis-(t-butyl)-2(dimethylbenzyl)phenol	
5	248	3,5-di-t-Butyl-4-hydroxyacetophenone	
6	324	2,6-Bis(t-butyl)-4-(dimethylbenzyl)phenol	
7	330	2,4-Bis(dimethylbenzyl)phenol	
8	386	2,4-bis(dimethylbenzyl)-6-t-butylpenol	
9	448	2,4,6-Tri(dimethylbenzyl)phenol	

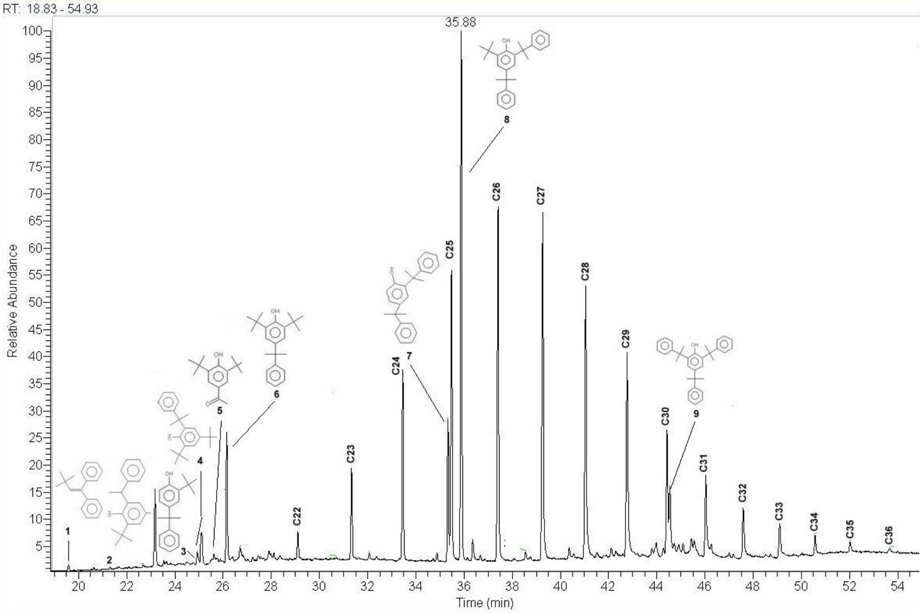

Fig. 1. *GC/MS chromatogram of the well water sample. Peak 1-9 are identified in Table 1. The peaks C_{22}-C_{36} are the hydrocarbons with the number of carbons in the range 22-36*

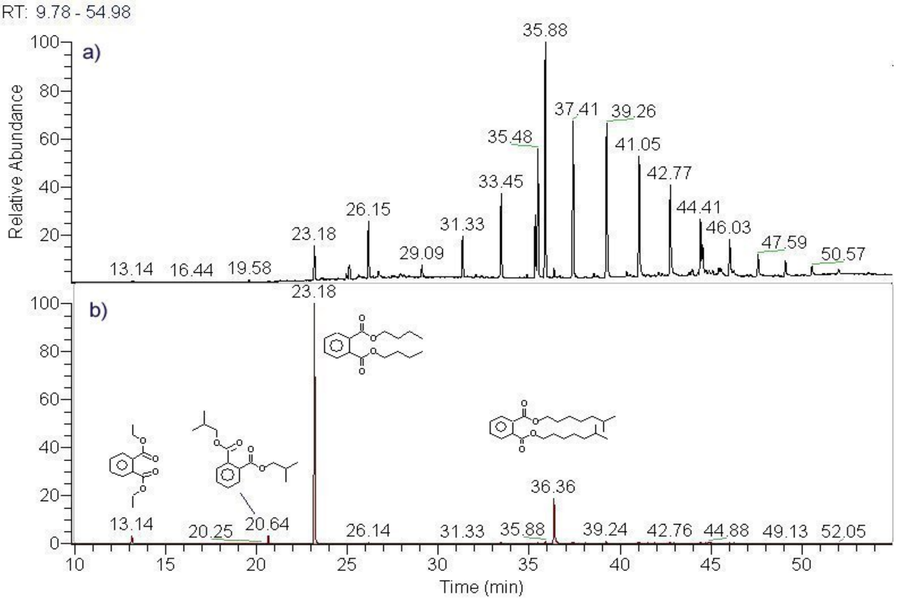

Fig. 2. *Detection of plastic additive (plasticizers) in studied water sample; a) TIC chromatogram; b) Characteristic ion chromatogram to m/z 149: Diethylphtalate (t=13.14), Diisobutylphtalate (t=20.64), Dibutylphtalate (t=23.18), Diisooctylphtalate (t=36.36).*

Plastics and other polymeric materials have become indispensable in our everyday lives. Although they offer many benefits, hazardous chemicals may be present in these materials. These hazardous materials can be introduced either intentionally as additives, or unintentionally as pollutants (AccuStandard, 2013). Therefore the plastic materials can be a significant source for new and emerging pollutants. The plastic additives are used for production of plastics with particular application as: Medical Devices, Food Packaging, Pharmaceutical Packaging, Toys, Wire and Cable, etc. Plastic additive are of following types:

a) Antioxidants work to slow down the oxidation cycle, usually by scavenging free radicals. (organophosphites, sterically hindered phenols, amines, and thioesters);

b) Accelerators (promoters) are additives that accelerate or speed up the chemical reaction or the curing of the polymers into the final plastic;

c) Antifoaming agents act to stop foaming during processing. Antifoaming agents typically work by reducing surface tension breaking up the foam;

d) Antidegradants include a broad category of additives used in compounding to slow deterioration that can occur due to oxidation, ozone or light;

e) Antiozonants are materials added to plastics to slow the deterioration of the finished product that occurs from exposure to ozone;

e) Blowing agents are sometimes also called chemical foaming agents. They are used to release gas into the plastic or resin. Blowing agents can be used to reduce weight, improve softness, provide insulation, add shock absorption properties or add resilience in the final product;

f) Coupling agents promote the physical or chemical interaction with the polymer;

g) Crosslinking is the polymerization reaction that branches out from the main molecular chain forming a network pattern of chemical bonds;

h) Crosslinking adds desirable properties such as: solidity, elasticity, impermeability to gases, and better electrical insulation;

i) Flame retardants are added to inhibit ignition or the flammability of the end-use product. Flame retardants generally function by inhibiting the mechanisms of burning;

j) A plasticizer is a compound added to a material, usually a plastic, to make it flexible, resilient and easier to handle. Plasticizers are major components in plastics that determine the physical properties of polymer products;

k) Biphenols are endocrine disrupters that exhibit hormone-like properties. This raises concerns about their use in polycarbonate based household products as well as medical devices;

l) Processing aids are compounding materials that improve the processing of polymers. (Reducing powder consumption during mixing, promoting compound fusion, adding lubrication, improving knitting);

m) Retarders are used to delay the onset of crosslinking and can be used to allow for longer processing times. They are also used to reduce scorching;

n) UV stabilizers, or light absorbers, act to protect the plastic against UV or sunlight damage such as discoloration, cracking, brittleness, or other loss of desirable physical properties;

o) Dyes and colorant products are one of the largest categories of plastic additives and are also used in textiles, leather goods, food and personal care products.

The petroleum additive industry is developing technologies and materials for the supply of service products for engines and motor vehicles, in cooperation with the petroleum and automotive industries, amongst others. While the activities of the industry are very well known on oil industry is very little public literature available. As a result, it is a need to know more about oil industry and particularly its impact on the environment (ATC, 2007).

The lubricant additives are produced with following purposes: friction reduction, corrosion protection, heat transfer, operating at extremes of temperature, engine seals protection, suspension of crankcase oil contaminants and viscosity regulators.Main chemical families of lubricant additives are (Yeomana et al., 2017):

a) Sterically hindered phenols;
b) Hindered Diphenylamines;
c) Zinc dithiophosphates (ZDDPs);
d) Phosphorus compounds;
e) Polysiloxanes.

CONCLUSIONS

Heavy rainfall events, impact drastic the quality of the surface water and water resource used for drinking-water.

The study of water sample collected from a drinking water well shows the presence of lubricants additives and plastic additives as pollutants. The presence of emerging pollutants in drinking water source is the result of agricultural, urban and industrial activities in the basin jointly with extreme rainfall.

This study focuses in an important aspect of the EU planning approach (regarding water quality and changes on water directives) due to extreme events. Implementation of suitable monitoring tools and procedures must to be planned with a view to a better knowledge of water-quality variation for a complete risk assessment and management program.

The increasing pollution by meteorological events leads to conclusion that for o good water management, the development of decision-support systems (DSSs) could be very advantageous in cases of extreme rainfall events. Finally, to respond and to react adequately to the crisis, analytical data need to be transferred to water managers for relevant, accurate decision making. DSSs represent the solution of the future, and are beginning to be employed in the drinking-water supply sector.

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COMPARATIVE STUDIES REGARDING THE USE OF RECYCLED PVC IN FINITE PRODUCTS

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ABSTRACT. The PVC wastes generated by post-industrial and post-consume activity creates serious problems regarding their wastes management. In the last years, the concept of reusing these wastes in other finite products became very attractive due to some advantages such as: eliminate the problems of their storage, decrease the price of the products in which these wastes are enclosed, and protect the environment against pollution. This paper presents some comparative studies regarding the use of recycled PVC in finite products such as obtaining PVC multilayer pipes. The quality and performances of the new products were compared with products in which only virgin PVC is used. The results showed that the quality of the finite products which contained recycled PVC is comparable with those of virgin PVC. Thus rigidity, flexibility, dimensional variation and shock resistance are similar or even superior if we use recycled PVC as raw material. The conclusion is that recycled PVC can be successful reused for obtaining PVC multilayer pipes being suitable to use in a percentage of 30-50%. Moreover, the economical benefices of this method are considerable.

Key words: *recycled PVC, finite products*

INTRODUCTION

Poly vinyl chloride (PVC) is one of the most widely used thermoplastic materials in terms of world polymer consumption. Globally, the demand for PVC exceeds 35 million tons per year and is ranked third, after polyethylene, which is the leading volume in the plastics industry, and polypropylene (Garcia et al., 2006, Yarahmadi et al., 2003). Due to the particular inherent properties of PVC, namely its low cost and high performance, combined with a wide range of products that can be obtained through different processing conditions and processes, PVC has become universal polymer (Braun, 2001).

Due to it specific proprieties, PVC can be processed currently in a wide variety of short-lived products such as packaging materials used in food industry, cleaning materials, textiles, beverage packaging bottle, various medical devices and also long-life products, such as pipes, joinery profiles, cable insulation, parquet, roof profiles, etc. (Matuschek et al., 2000).

By comparison the total amount of the polymers used surround the world it can be observed that PVC is the fourth used polymer after polyethylene, polypropylene and polystyrene (figure 1).

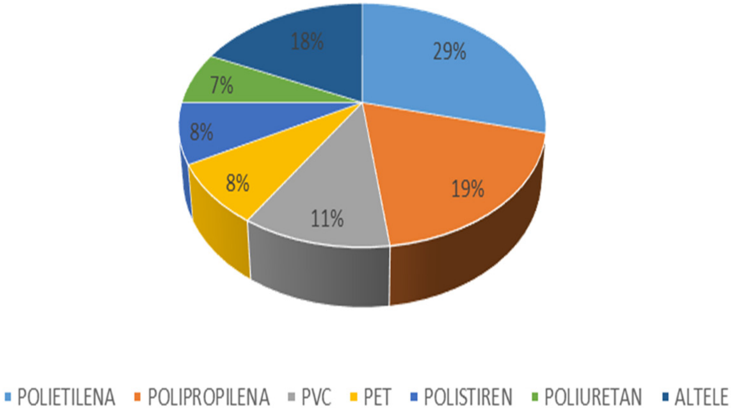

Fig. 1. *Distribution of plastic mass processing*

In the last years, the PVC waste disposal has gained increasing importance because the PVC waste has been a rapid increase and the place of their disposal is limited. Moreover, even the long-lasting PVC products have a long-life span and there is a long time between PVC consumption and the accumulation of PVC waste, they will become waste in time (Braun, 2002).

Thus, the finding ways to reuse of PVC waste has become a priority. In the last time, the researches having as subject the reuse of PVC waste have strongly increased (Garcia et al., 2007, Burat et al., 2009). As a result, the quantity of articles made of PVC introduced into the waste stream is gradually increased as the progressive number of PVC products is approaching the end of their useful economic life (Nakamura et al., 2009, Patel et al., 1998, Patel et al., 2000).

According to Vinylplus (https://vinylplus.eu) the amount of PVC waste reused in different finite products has gradually increased and in 2016 more than 568 thousand tons of PVC wastes were reintroduced in technological fluxes.

Of course, it is not enough to recycle the PVC waste, it is important that the recycled waste to be reused in commercially available products, close to the initial use range. In the last time, different products and technologies have been developed to efficiently absorb these wastes (Sambatsompop et al., 2001). A short radiography of PVC waste reuse showed that it can be successfully used in various products the most important being windows profile and related products (46%), cable (21%), mixed flexible PVC applications (19%), pipes and fittings (10%) or rigid films (4%).

The aim of this study was to compare the quality of two different multi-layer pipes, one obtained from virgin PVC and another containing micronized recycled PVC.

Obtaining PVC multi-layer pipes for indoor or outdoor sewers that contain a micronized recycled PVC middle layer made from pipe waste, fittings, joinery profiles or technical profiles is one of these applications Recycled micronized PVC goes through all stages of mechanical recycling, being brought to a pulverizing form by micronizing scraped waste.

PRODUCTS, PROCESS AND METHOD

Micronized recycled PVC waste can be used in compact PVC pipes used for sewage systems, both inside and outside buildings and using industry standard values, namely:

- at external diameter we have values in the range 110 - 500 mm, with a tolerance between 0.3-0.9 mm,
- for the stiffness class SN 2, SDR 51, the wall thickness is between 2.2-9.8 mm with a towel between 0.5-1 mm,
- for the stiffness class SN 4, SDR 41, the wall thickness is between 3.2-12.3 mm with a towel between 0.6-1 mm,
- for the stiffness class SN 8, SDR 34, the wall thickness is between 3.2-14.6 mm with a towel between 0.4-1.4 mm,
- For the rigidity class SN 12, SDR 30, the wall thickness is between 10.3-16.5 mm with a towel between 1.2-1.7 mm.

Typically, these pipes are obtained by extrusion process using a manufacturing recipe in which the base raw material is PVC with a K value between 64-68, plus Ca-Zn-based stabilizers and lubricants so that we can process the material.

The production recipe is made with the help of dosing and mixing plant, the raw materials dosed after certain proportions are introduced into the mixer, are mixed up to a temperature of 110-130^0 C, after which the mixture is cooled to a temperature of 40-50^0 C, with the help of a cooler. The mixture is stored in bunkers from where it is fed to the production lines.

A PVC pipe extrusion line consists of an extruder, a mold, a calibration/ cooling valve, a tracer, a circular and a dowel.

Micronized Recycled PVC Coated Pipes consist of 3 layers, 2 of the layers are inside and outside and are of virgin PVC and the middle layer is made of micronized recycled PVC (figures 2 and 3).

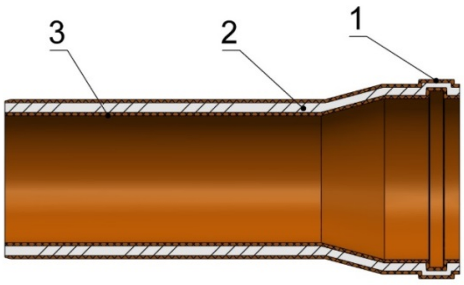

Fig. 2. *Multilayer pipe - cross section*

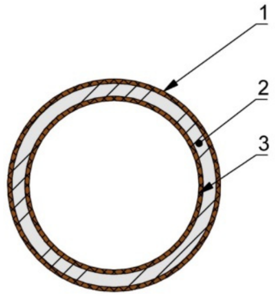

Fig. 3. *Multilayer pipe - horizontal section*

These are obtained by the same extrusion process using manufacturing recipes with identical compositions, the difference being the first raw material used. The extrusion line in this case will consist of an extruder for the micronized recycled PVC middle layer and a co-extruder for the inner and outer virgin PVC layers. The layers are joined in the specially designed die.

Practically, compact PVC virgin K 67 tubes of the SN4 and SN8 stiffness class of 250 mm and 315 mm diameters were extruded using an L/D (length across diameter) extruder =26 and a non-feed block die (sample 1) and micronized recycled PVC medial multilayer (maximum particle size 1400 µm) using an L/D =26 extruder and co-extruder and a feed block die. The proportions used were 70% - 30% (inner layer - exterior with virgin PVC versus medium micronized recycled PVC layer, sample 2), 60% - 40% (interior varnish layer with virgin PVC versus medium micronized recycled PVC layer, sample 3) and 50% - 50% (inner-outer layer with virgin PVC versus medium micronized recycled PVC layer, sample 4). The extrusion temperatures set on the cylinder areas ranged between 170-180^{0}C and on the mold 180-2000C and the manufacturing recipe used was the standard one (Table 1).

Table 1. *Standard recipe*

VIRGIN PVC LAYER		**MICRONIZED RECYCLED PVC LAYER**	
PVC K 67	83.5%	MICRONIZED RECYCLED PVC	83.5%
CALCIUM CARBONATE	12.5%	CALCIUM CARBONATE	12.5%
STABILIZER CA-ZN	2.9%	STABILIZER CA-ZN	2.9%
POLYETHYLENE WAX	0.2%	POLYETHYLENE WAX	0.2%
CHLORINATED POLYETHYLENE	0.8%	CHLORINATED POLYETHYLENE	0.8%

RESULTS

The samples taken from the tests were subjected to specific determinations such as shock resistance, dimensional variation after heating at 150 °C, ring stiffness and ring flexibility. The obtained results are centralized in the tables 2.

As can be seen in Table 2, ring rigidity increases with the increase in micronized recycled PVC content, and for flexibility, the forces increase without adverse effects on the pipes. We do not break the hitting of pipes with standard weight, handling under site conditions can be done without any problems. Dimensional variation is below the required limit.

Table 2. The results obtained for the tested pipes

PIPE TYPE SN4 250								
No.	**The determined feature**	**Standard**	**UM**	**Standard requirement**	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**
1	Determination of shock resistance by free fall	SR EN 744:2003	%	TIR < 10	Without burglary	Without burglary	Without burglary	Without burglary
2	Determination of dimensional variation after heating at 150 ° C	SR EN ISO 2505:2005	%	< 5	4.2	3.2	3.1	3.3
3	Determination of ring stiffness	SR EN ISO 9969:2016	Kpa/m^2	4	4.47	4.6	4.7	4.75
4	Ring flexibility	SR EN 13968:2009	N	Force to 30% deformation	2806	2850	2886	2912
PIPE TYPE SN4 315								
No.	**The determined feature**	**Standard**	**UM**	**Standard requirement**	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**
1	Determination of shock resistance by free fall	SR EN 744:2003	%	TIR < 10	Without burglary	Without burglary	Without burglary	Without burglary
2	Determination of dimensional variation after heating at 150 ° C	SR EN ISO 2505:2005	%	< 5	3.4	3.55	3.7	3.75
3	Determination of ring stiffness	SR EN ISO 9969:2016	Kpa/m^2	4	4.65	4.7	4.8	4.85
4	Ring flexibility	SR EN 13968:2009	N	Force to 30% deformation	3244	3350	3376	3396

PIPE TYPE SN8 250

No.	The determined feature	Standard	UM	Standard requirement	Sample 1	Sample 2	Sample 3	Sample 4
1	Determination of shock resistance by free fall	SR EN 744:2003	%	TIR < 10	Without burglary	Without burglary	Without burglary	Without burglary
2	Determination of dimensional variation after heating at 150 ° C	SR EN ISO 2505:2005	%	< 5	3	2.75	2.8	2.85
3	Determination of ring stiffness	SR EN ISO 9969:2016	Kpa/m^2	8	8.88	8.92	8.95	8.98
4	Ring flexibility	SR EN 13968:2009	N	Force to 30% deformation	4542	4596	4612	4628

PIPE TYPE SN8 315

No.	The determined feature	Standard	UM	Standard requirement	Sample 1	Sample 2	Sample 3	Sample 4
1	Determination of shock resistance by free fall	SR EN 744:2003	%	TIR < 10	Without burglary	Without burglary	Without burglary	Without burglary
2	Determination of dimensional variation after heating at 150 ° C	SR EN ISO 2505:2005	%	< 5	3.4	3.21	3.15	2.95
3	Determination of ring stiffness	SR EN ISO 9969:2016	Kpa/m^2	8	8.62	8.67	8.72	8.75
4	Ring flexibility	SR EN 13968:2009	N	Force to 30% deformation	5472	5483	5491	5508

CONCLUSIONS

It can be seen that the results obtained for the micronized recycled PVC medial tubes are better than the virgin PVC pipes, the benefits being an effective recycling of this waste with a positive impact on the environment and a lower cost of raw materials.

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CONTRIBUTIONS OF THE SCIENTISTS FROM CLUJ TO THE COSMIC SPACE RESEARCH

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ABSTRACT. It is now widely accepted that modern investigations for research of complex processes occurring in the atmospheres of the planets began on Oct. 4, 1957 with the orbiting of the Earth's first artificial satellite. With the launch of the first rockets and satellites in space, there are "unexpected" discoveries world-wide in this domain. Thus, in 1958, van Allen radiation belts around the Earth (Henry Elliot, 1959) were discovered, which led to the launch of laborious scientific programs for the study of Earth's Higher Atmosphere in all aspects (electrical, magnetic, chemical, etc.). Investigation of neutral and ionized constituents from upper atmosphere of the Earth represent an important parameter for solving some geophysical and astrophysical problems. For example, atmospheric pressure and temperature can not be accurately measured or determined without knowing very well the composition of the neutral constituents. The problem of locating the gas gravity separation level can only be solved only after a detailed investigation of the neutral atmosphere composition. Knowing the structure of the atmosphere is the basic requirement for investigation of other physical processes from the Earth atmosphere. The work is a history of the main investigating institutes from Cluj-Napoca who were involved in the initiation, development and construction of equipment for the major investigate the outer space and for conducting observations of trajectories of artificial satellites.

Key words: *INCDTIM, Calibrator, Mass spectrometer, Nano balance, Deuterium, Lunar soil, Soyuz 40*.

INTRODUCTION

The mass spectrometers were used in the research laboratories as multi-purpose sensitive equipment capable of analyse quantitatively and qualitatively complex mixtures of gas, liquid and solid. It is not surprising that when high altitude missiles became available to research, mass spectrometers were sent to investigate the nature of the higher atmosphere.

In 1949, a mass spectrometer with magnetic field is built and installed on a V-2 type rocket, making the first measurement of the ratio between the numerical densities (particles/cm^3) of helium and argon up to the altitude of 130 km (O'Day, 1954). In 1953, a Bennett radio-frequency mass spectrometer is installed on an Aerobee rocket, and in 1959 on the Soviet satellite Sputnik 3 (Townsed, J.V., 1954). After 1960, these types of instruments are more frequently used for the measurements of upper atmosphere composition (Schaefer 1963). Simultaneously with the exploring of Earth's atmosphere, mass spectrometers are successfully used to investigate other planets from the solar system (Spencer, 1971, Hoffman, 1979, Istomin, 1983) and to investigate the Earth's natural satellite.

In this context, at the working meeting from 15-20 November 1965 in Moscow, delegations from eight socialist countries, including Romania, decided to set up and launch the INTERCOSMOS Program in order to cooperate for the peaceful exploration and use of cosmic space. The INTERCOSMOS Program was a replica of the American Space Research Agency (NASA). In 1968, the Inter-ministerial Commission CRAS (Romanian Commission for Spatial Activities) was founded, in order to coordinate the development of space activities at national level.

The initiative of including new areas of space research among the scientific domains of researchers from Cluj belongs to: Professor Dr. doc. Victor Mercea, Corresponding Member of the Romanian Academy, Director of the Institute of Isotopic and Molecular Technologies from Cluj (now INCDTIM) and Professor dr. doc. Gheorghe Chiş, director of the Astronomical Observatory from Cluj, as a consequence of their participation at the annual meeting of the Cosmic Physics Group from the INTERCOSMOS Cosmic Space Research Program in 1971.

One of the conclusions of this meeting was the necessity of building new equipment for the study of Earth's atmosphere and for the ground monitoring of the satellites paths found on orbit. On this occasion Professor V. Mercea proposes to be introduced as a future research, in INTERCOSMOS Program, the topic of calibration improvement of mass spectrometers from spatial objects, and the development and construction of a quadrupole mass spectrometer, which proved his efficiency in the experiments performed by Western countries. Professor Gh. Chiş proposed the involvement of the Astronomical Observatory of Babeş-Bolyai University from Cluj in these research activities.

The main research institutions from Cluj-Napoca, which have been involved in the realization of these themes, were:

- Institute of Isotopic and Molecular Technologies (current Institute for Research and Development for Isotopic and Molecular Technologies – ITIM) and
- Babeş-Bolyai University from Cluj-Napoca through the Faculty of Chemistry and the Faculty of Mathematics (Astronomical Observatory).

Since 1993, the private company BITNET-CCSS Cluj-Napoca was also involved in different space research activities.

RESEARCH ACTIVITIES PERFORMED AT ITIM CLUJ-NAPOCA

The participation of ITIM from Cluj-Napoca in the joint program for research and peaceful use of the cosmic space INTERCOSMOS began in 1972 by approaching two research topics regarding: (1) the mass spectrometers calibration during flight and (2) the construction of a quadrupole mass spectrometer for the research of Earth upper atmosphere.

Mass Spectrometer Calibration Device

Starting from the need to calibrate mass spectrometers installed on space objects, which can modify their characteristics during space flight, a research topic has been proposed on “Developing of a method and building of a device for calibration during flight of mass spectrometers installed on satellites or orbital laboratories”. The method used by Soviet specialists from the Moscow Cosmic Research Institute (I.K.I. - Moscow) consists in using the diffusion phenomenon of light gases through quartz membranes. The calibration gas should not be found among the atmospheric components which should be measured. Romanian specialists propose the replacing of the quartz membrane with a metallic membrane.

The device is composed of two distinct parts: a) the mechanical part, comprising the standard gas tank, the temperature sensor and the heating resistance of the tank; b) the electronic block providing the thermoregulation of the standard gas flow which pass through the stainless steel metallic wall, and it can be changed from the ground in two steps to 10^{-2} and 10^{-4} l/s and the sending of the data to telemetry system. The gas which comes out from the standard is directed to the ion source of the spectrometer which will be calibrated. The input time of the device is 5 minutes, consumes about 5 W and has a total weight of 0.7 kg. The operating principle is illustrated in figure 1 (Mercea Victor, 1975).

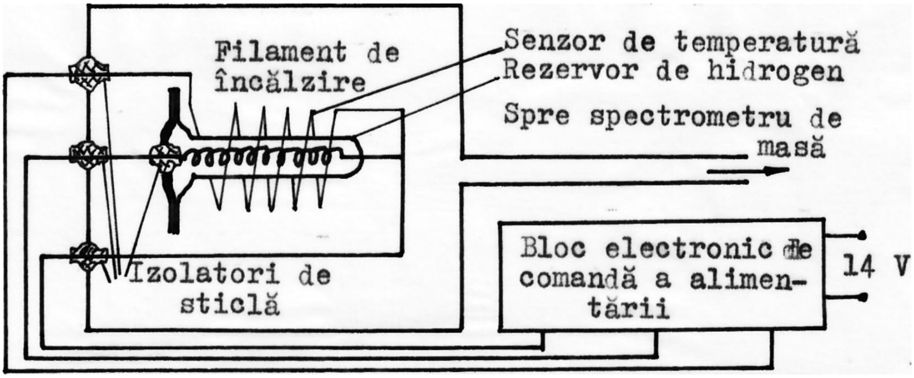


Fig. 1. *Schematic diagram of a device for calibration of mass spectrometers during flight.*

The first experiment with this device, called DESM-1, took place on the INTERCOSMOS-12 satellite launched on October 31, 1974 on the Plesetsk Cosmodrome located at 62.8 °N, 40.4 °E, figure 2.

Fig. 2. *The Cosmodrome from which the INTERCOSMOS 12 satellite was launched.*

The obtained results suggested the need to change the calibration gas due to the fact that over the mass spectrum of the calibrated gas, an unknown background spectrum is overlapping, which in some cases had very high values. Further research was carried out on the calibration method and on the instrument. Thus, DESM-3 uses deuterium as a filling gas, palladium membrane, has an entry regime time of one minute, consumes only 2.5 W and has a total weight of 0.150 kg.

Figure 3 shows the calibration curves of the two standard versions and a photograph of DESM-3.

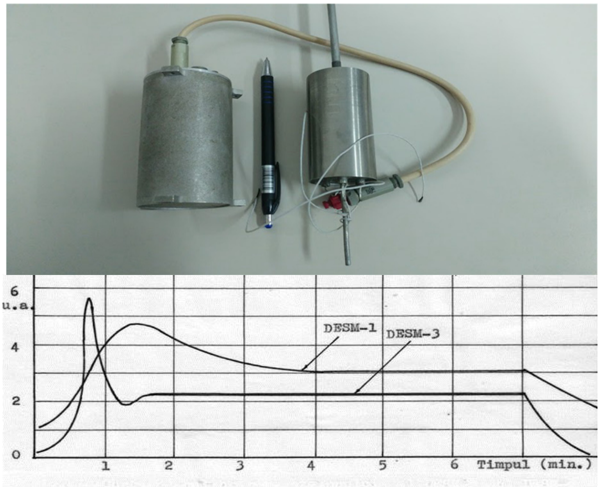


Fig. 3. *DESM-3 and the calibration curves of the two standards (entry regime time versus flux intensity)* (Mercea, 1975).

The DESM-3 device was installed on the INTERCOSMOS-18 satellite launched on October 26, 1978, on the Baikonur Cosmodrome, with great results. The weight of the device was reduced from 0.540 kg (DESM-1) to 0.125 kg (DESM-2) and power consumption from 9.2 watts to 6 watts.

Quadrupole mass spectrometer for the research of the isotopic composition of the upper atmosphere

The second research topic approached by ITIM Cluj-Napoca in 1972 was closely related to the diversification and improvement of mass spectrometry equipment. A radio-frequency mass spectrometer was installed and used for INTERCOSMOS. Other types of mass spectrometers have been successfully tested, worldwide, from which the mass spectrometers with magnetic field and quadrupole-type proved their performances. Starting from the advantages of the quadrupole mass spectrometers, compared to those with magnetic field, it was proposed to start the research activities in order to design a quadrupole mass spectrometer for the atomic and isotopic analysis of the major constituents of the upper atmosphere of the Earth.

The main advantages of this type of spectrometer are: low weight, high robustness, linear mass range, high sensitivity, low power consumption. Figure 4 shows a simplified scheme of the QMS-3 spatial mass spectrometer and in figure 5 it is shown its construction scheme (Ristoiu D., 1980).

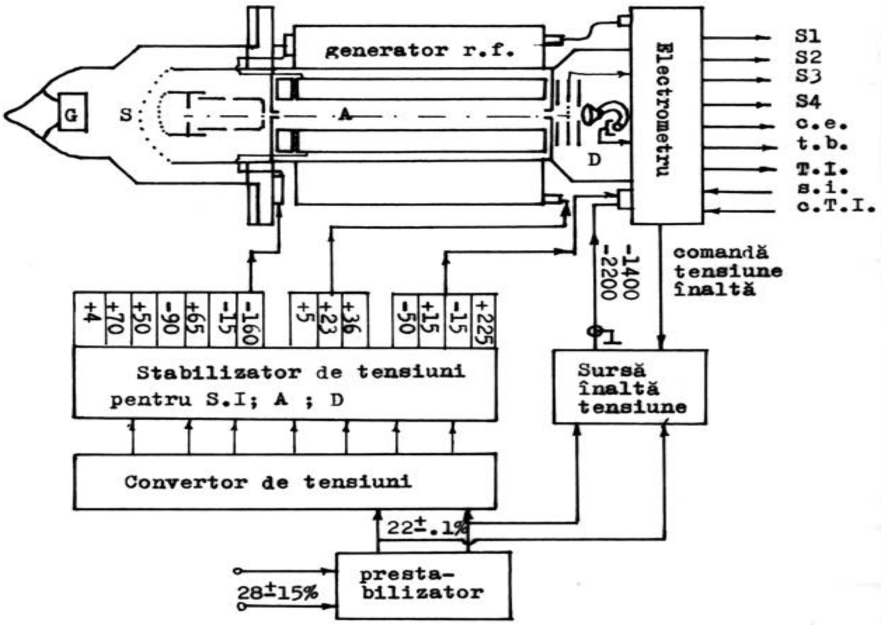


Fig. 4. *Simplified diagram of quadrupole mass spectrometer with spatial destination and its electronic block (Ristoiu D., 1980).*

The laboratory model of this instrument was put into operation in 1975 and has the following working parameters: the mass range 1 - 55 uam, resolution of 200 at 1/2 of the height of the mass peak, sensitivity of 10^{-4} A / torr with Faraday collector and 1 A / torr with secondary electron multiplier, dynamic range 10^{6} covered in 4 steps, maximum power consumption 20 W, total weight 12 kg.

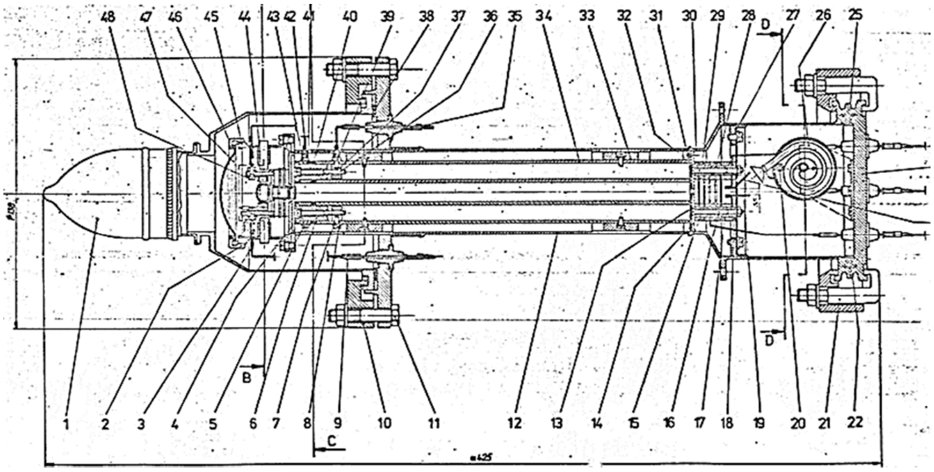


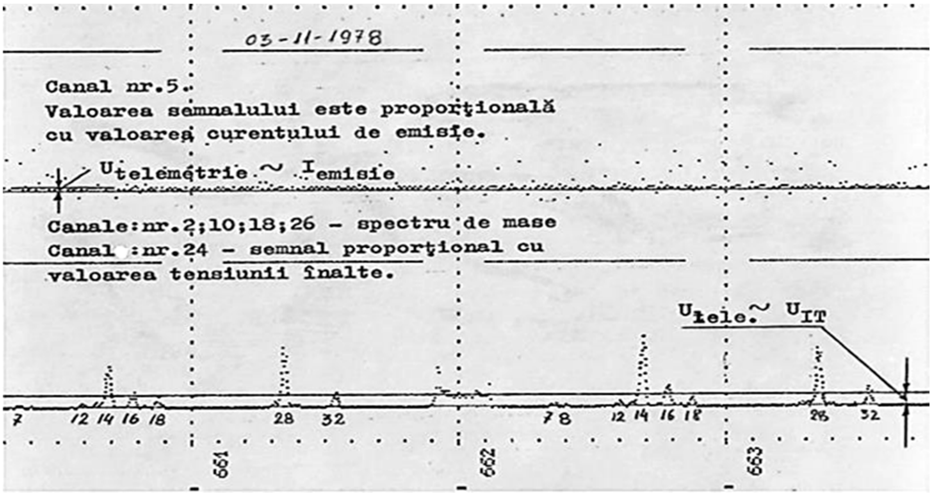
Fig. 5. *Scheme of construction of QMS-3 (Ristoiu D., 1980).*

By redesigning some subassemblies of the apparatus, a technological model has been achieved that has a performance similar to laboratory model but consumes less power (15 W) and has a lower weight (7.5 kg), the mass spectrometer SMQ-1 was launched on the high altitude geophysical rocket Vertical 7 in November 3 1978 and worked well with the following flight performance: mass range 1-40 uam, resolution 100 at 1/2 of peak height, sensitivity of 10^{-4} A / torr for Faraday collector and 1 A / torr for the secondary electrons multiplier, dynamic range 10^{5}, average power consumption 12 W, total weight 6.3 kg.

The main atomic and molecular species detected in the mass spectra were: H^+, H_2^+, N^+, O^+, N_2^+, O_2^+ and as ground-based impurities H_2O^+ and OH^+, figure 6 (Ristoiu D., 1980).

In order to improve the working performance of the device, for a new release, the ionic current detection system and the vacuum shutdown of the device were modified. For the technological and pre-launch samples the device was equipped with an own vacuum system based on an ion pump with a pumping speed of 10 l/sec. This version was called QMS-3. During the technological tests carried out at IKI-Moscow and the Cosmodrome in April 1980, the device proved to be reliable with substantially improved results (Toderean G., 1979). This type of spectrometer was launched on VERTICAL 9 and 10 rockets.

Figure 7 shows the standard container on which was installed the scientific equipment on VERTICAL rocket (top left) and fly version of QMS-3 (bottom left- electronic block and right- mechanical side).



03-11-1978

Canal nr.5.
Valoarea semnalului este proporţională
cu valoarea curentului de emisie.

$U_{telemetrie} \sim I_{emisie}$

Canale:nr.2;10;18;26 – spectru de mase
Canal :nr.24 – semnal proporţional cu
valoarea tensiunii înalte.

$U_{tele.} \sim U_{IT}$

Fig. 6. *Two-channel recording sequences.*

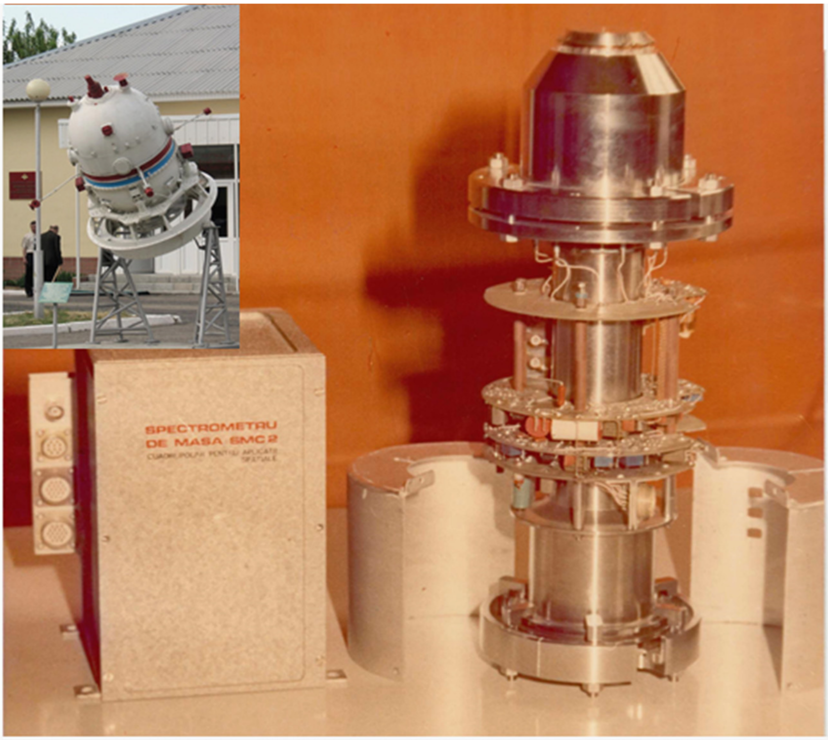


Fig. 7. *Mass Spectrometer QMS-3. The electronic block (bottom left), the container (top left) and the mechanical part of the QMS-3 (right) on which is installed the radio frequency generator and the electrometer.*

The success of this experiment, designed and built entirely at ITIM and successfully launched in space, places Romania among the top six countries in the world that build mass spectrometers for space research. The team's success was rewarded by awarding the Gold medal to the QMS-3 spectrometer at the Moscow National Exhibition of Achievements of the National Economy 1987, for "Cuadrupolar Mass Spectrometer for Spatial Applications" Figure 8.

Постанов. от 3 июня 198 7 г.
№ 416-Н

УДОСТОВЕРЕНИЕ
№ 1599

за достигнутые успехи в развитии научно-технического сотрудничества социалистических стран

Главный комитет ВДНХ СССР
НАГРАЖДАЕТ
ЗОЛОТОЙ
МЕДАЛЬЮ

Экспонат Квадрупольный спектрометр для пространственных применений

Автор

ГЛАВНЫЙ КОМИТЕТ

Главный комитет Выставки достижений народного хозяйства СССР

Fig. 8. *Gold medal, assigned by Decree 416-N / 03.iunie 1987 Certificate Number. 1599, at the "National Economy Exhibition" USSR, Moscow.*

MARS '94 PROGRAM

It was launched in February 1987. ITIM Cluj-Napoca participates with two experiments

1. "Study of the structure and isotopic composition of the high atmosphere of Mars using mass spectrometry", abbreviated **SCIAPM**. The purpose of the experiment was to obtain global information about the concentrations of neutral and ionized constituents and their isotopic ratios in the high atmosphere of Mars
2. Piezoelectric Hygrometer

The SCIAMP experiment

In the case of Mars, as well as in the case of the other planets, the knowledge of the atmosphere composition and especially of isotopic ratios is very useful for the explanation of the genesis and evolution of the atmosphere. The importance of the physical and chemical processes which are playing a major role in the state of the atmosphere, can be obtained by isotopic data.

The mass spectrometry is the most important and versatile method for isotopic - ratios measurements (Prolss, 1974, Mercea V, 1978). Taking account of the accuracy of double collector methods, used for the mass spectrometer isotopic analysis, a device consisting of twin quadrupole mass spectrometers is .proposed (Ristoiu, 1991).

The use of mass spectrometers devices in the planetary missions was very useful for the study of planetary atmospheres of the Earth, Venus, Mars and Jupiter (Surkov 1957). The device consisting in the use of the double collector method was realised by the simultaneous use of a pair of quadrupole mass spectrometers. Such a mode of operation of the device can resolve some problems like those appearing in the case of quick commutation of the range of ionic current measuring systems, quick temporary variations of the pressures and bulk variations of the electronics.

The geometry of the twin quadrupole mass spectrometers is identical.

In order to tune one of the cuadrupolar mass spectrometer on the mass m a potentials $\pm(U + V.cos\omega t)$ are applied on the rods of mass analyser. For given a and q — operating parameters — the magnitude of U.and V can be deduced from the relations [7]:

$$a = \frac{8eU}{mr_0^2\omega^2} \qquad q = \frac{4eV}{mr_0^2\ \omega^2}$$

In these relations: e - electron charge, r_0 - radius of the quadrupole field, ω - operating frequency of the mass analyser. For the tuning of the other quadrupole mass spectrometer, on the mass $m + k$ the potentials $(U' + V'\ cos\omega t$ must have $U' = U(1 + k/m)$ and $V' = V(1 + k/m)$.

Until the contributions of the ions having masses $m + k - 1$ and $m + k + 1$ does not give remarkable contributions to the peak of the ions of mass $m + k$, one can decrease the mass resolutions in order to obtain higher ionic currents. The operations of device is done and controlled by micro computerized electronic unit.

After the dissolution of the Soviet Union in 1991 the project was abandoned.

The construction of the device is presented in Fig 9.

The Piezoelectric Hygrometer experiment

The working principle of this device consists of changing the fundamental frequency of vibrating piezoelectric quartz crystal, when a change of the mass of a thin film deposited on its surface, occurs. Such a change of the film mass may be obtained by absorption of gasses or vaporous which are present in the quartz crystal monitor environment. The piezoelectric hygrometer consists of such a quartz crystal covered with a thin hygroscope layer. This quartz crystal drives the frequency of an oscillator, which may be measured at the output, with a digital frequency meter.

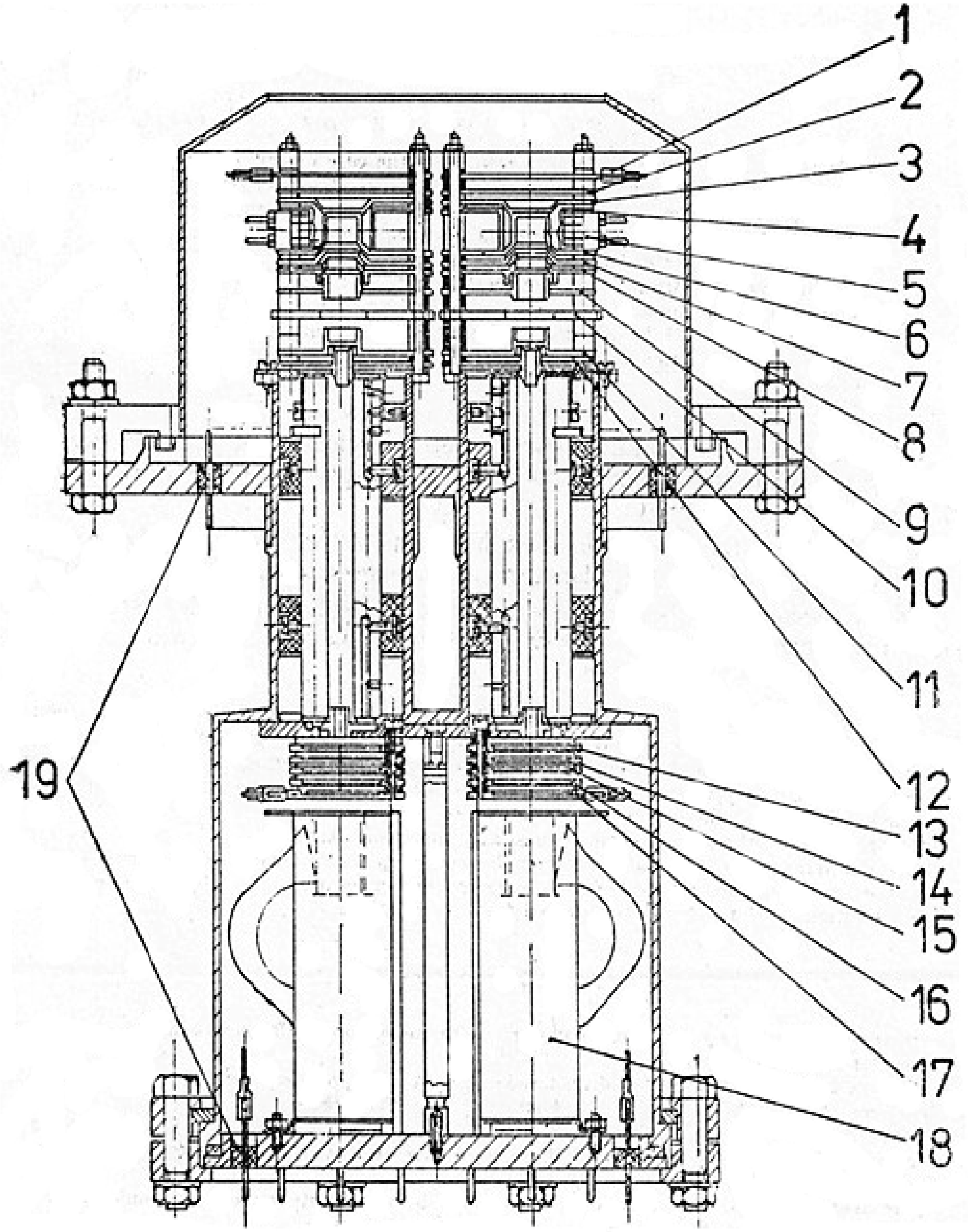


Fig. 9. *The MARS '94 spectrometric device. 1, 2, 3 — grids, 4 — electron lens, 5 — filament ensemble, 6 — ionization chamber, 7 — extraction grid, 8,9 — ion lens, 10 — retarding potential analyser,11 — total ion current collector, 12 — entrance aperture, 13, 15, 17 — screen grids, 14, 16 — ion collector grids, 18 — channeltron electron multiplier, 19 — feedthroughs (Ristoiu 1991).*

In order to overcome the unwanted effects, mainly that of the temperature, on the unwanted effects, mainly that of the temperature, on the quartz crystal frequency, the addition of an identically quartz - oscillator system, having an uncovered reference quartz, is proposed. The measured signal will be the electronically operated frequency difference between the two quartz crystals.

Performances: Measuring range: 1 - 30,000 ppm water, (unlinear, more sensitive at lower concentrations); Working temperature range: -40 - + 80 °C; Power consummation: - 1 Watt; Weight: - 500 g.

ANALYSIS OF SOIL SAMPLES FROM THE MOON

Taking into account both the equipment from the Mass Spectrometry Laboratory at ITIM Cluj-Napoca and the methodology for physico-chemical analyses, since 1974, a new research topic was studied that proposed “The study of the gases in samples of lunar soil”. For this, the Soviet side provided the ITIM scientists with 0.5 grams of lunar soil samples that were analysed in order to determine the content of rare gases. To perform these analyses, an installation for the extraction of gas from the samples was designed and a method of static analysis of the gases contained in the soil samples was elaborated. Of particular significance from the point of view of the planet’s genesis is the ratio of the isotopes of Argon: ^{40}Ar (99.6%), ^{36}Ar (0.34%) and ^{38}Ar (0.06%). The obtained results confirmed the common origin of the Moon and Earth soil.

EXPERIMENTS PROPOSED BY THE ROMANIAN COSMONAUT DUMITRU PRUNARIU ON THE SOYUZ-40

Nano-balance

Since 1974, a new theme has been dealt regarding the development of an instrument for the determination of humidity in planetary atmospheres in order to detect water traces from other planets atmosphere. The device was based on a very sensitive piezoelectric balance capable of detecting water in quantities of up to 10^{-9} grams. It was originally designed to measure the water vapour content of the Mars or Venus atmosphere in 1975. Due to the short term, the destination of the experiment was changed. Later, this microbalance was perfected and proposed as an experiment at the Soyuz-40 orbital station with a Romanian cosmonaut on board, in order to study the erosion of protective layers under cosmic conditions; the experiment was “NANOBALANCE”.

In principle, the instrument consists of two piezoelectric resonators installed on the same crystal, from which one is subjected to cosmic agents. Frequency changes resulting from the change in mass of the investigated protection layers are recorded and sent to the ground.

The purpose of the experiment was to obtain information on the stability of thin silicon dioxide protective layers under the influence of the cosmic environment (radiation, vacuum, etc.). In this way, it can be seen how long resist a thin layer of silicon dioxide deposed on the surface of some optically active elements located outside the space laboratories, such as solar cells. Such layers have a remarkable chemical resistance and have the advantage of being transparent in a very wide spectral range.

The research apparatus that served to NANOBALANCE experiment weighs with high precision and very high sensitivity of 10 ng, the mass of a thin layer deposited on the surface of the sensor made up of a quartz resonator. The degradation of this thin layer of silicon dioxide translates into the modification of the vibration frequency of the quartz resonator, which is measured by the apparatus and then is transmitted to the Earth.

The experiment was carried out by exposing the sensor to the cosmic environment for a specified time, after which, at a command sent by the cosmonaut, the sensor closed and the frequency change occurred as a result of the cosmic action on the protective layer of the dioxide silicon.

In addition to the autonomous block, the device also includes a command and control board used by the cosmonaut.

By implementing the NANOBALANTA technological experiment, particularly useful results were expected that could reduce the weight of solar cells and prolong the duration of their use by applying thin layers of silicon dioxide on their surface.

DEUTERIUM experiment

Global measurements with mass spectrometers installed on spatial objects reveal large discrepancies between the results obtained by different groups of researchers. In order to discover the nature of these discrepancies, it was proposed to produce a quadrupole mass spectrometer, type QMS-3, equipped with two calibration devices which could be operated alternately during flight by the cosmonaut. One of the standards will use hydrogen and the second will use deuterium. In this way one can study the systematic and memory errors of space-mass spectrometers.

The research team proposes to test the SMO-3 quadrupole mass spectrometer under real working conditions for its usage in measuring the ratio of hydrogen isotopes to a reference unit. Direct measurement of atomic hydrogen is difficult due to its very high chemical reactivity. Various experiments mentioned abnormal hydrogen behaviour and an H / D ratio very different from the one known on the ground.

In order to correct the results obtained by direct measurements it was proposed to study the photochemistry and recombination reactions of H and D in the ion source of the spectrometer under evolution conditions of spectrometer on a spatial object. Aspects of Romanian Cosmonautics visit to Cluj Napoca are shown in Figures 10 and 11.

Fig. 10. *Visit of Cosmonaut Dumitru Prunariu at ITIM 1983.*

Fig. 11. *Visit of Cosmonaut Dumitru Prunariu at UBB, 2014.*

Measuring the isotopic distribution of hydrogen versus the altitude provides first of all information on hydrogen dynamics and secondly information on the origin and genesis of hydrogen on Earth.

Due to the complexity the required equipment, the experiment could not be finished on time.

RESEARCH ACTIVITIES PERFORMED AT UBB CLUJ-NAPOCA

Faculty of Chemistry. In 1978 Prof. dr. Emil CHIFU proposes the topic: The superficial liquid leakage in the absence of gravity, to be carried out in collaboration with the NASA - National Aeronautics and Space Administration - USA. Theme consisted of two experiments; a) The surface leakage between the two surfaces joined by shallow channels; b). Superficial leakage on a liquid drop. After a rigorous selection process by NASA, the two experiments had been accepted to be tested in outer space (Tomoaia-Costișel, 2007).

It is very interesting that although the teacher Chifu - which, for reasons unknown, was not allowed to leave the country, although he was always invited by NASA to participate in the realization of his project - he keep in touch (through the post office) with the Jet Propulsion Laboratory team of researchers that built the experiment model and implemented on DDM (Drop Dynamics Module) module in NASA's 3rd Lab Space Lab 3 (1981).

Faculty of Mathematics. The Astronomical Observatory is an educational and research institution in fields such as general astronomy, astrophysics, celestial mechanics, and artificial satellites.

Satellites are very complex machines that require precise mathematical calculations in order for them to function. There are number of scientific reasons for wishing to have an easily visible satellite. In particular, precision orbit determination will probably be done optically, and it is clearly desirable to have a satellite which reflects or emits a considerable amount of light. An available method is the creation of a large reflecting object such as a metal balloon, Figure .13.

Precision orbit determinations based on optical tracking can be used for: a) Determination of air drag at high altitudes, from which atmospheric density can be derived, b) A possible complication is the effect of an electrostatic charge on the satellite, and the interactions between this charge, the ions present in the ionosphere, and the Earth's magnetic field, c) Geodesic measurements on the size and shape of the Earth, d) Ion densities, when coupled with certain precision radio techniques.

The launch of Earth's artificial satellites, started in 1957, opened new possibilities for collaboration to the Cluj-based astronomy. The two satellite tracking and observation stations in Cluj and Bucharest begin close collaboration with similar research centres like the USSR and the US.

The college of researchers at the Astronomical Observatory of UBB (Faculty of Mathematics) takes part in making systematic observations on the “brilliant” satellites Echo I and Echo II, as well as on the cosmic triangulation operations carried out between 1963 and 1964.

Fig.12. *Pageos, balloon satellite.*

Fig. 13. Astronomical *Observatory of UBB.*

With the launch of the INTERCOSMOS Program, the activities of the team extend to the observation and tracking of the “brilliant” satellites launched by the USSR.

RESEARCH ACTIVITIES PERFORMED AT BITNET-CCSS CLUJ-NAPOCA

BITNET-CCSS is a small private company, which is active since 1993 in the field of technological research & consulting.

Main research and business areas: applications of satellite communications, small radiotelescopes, prototype surveillance of space sensors (optical and radio) and information technology.

BITNET is involved in the development of the Romanian space program and has completed more than 50 R&D projects until today, many of them in partnership with Romanian authorities, universities, research institutes or other companies. BITNET is involved in space related international projects and activities, including cooperation with ESA and NATO. The figure 14 show a part of infrastructure of Company.

Fig.14. *Our test infrastructure for satellite communication and surveillance of space experiments – in development. Located in Marisel, 1150 m altitude, 50 Km far from our offices in Cluj-Napoca. Electromagnetic quiet zone and without light pollution. The test bed hosts BITNET's astronomical observatory and several antennas covering different radio bands, from few Hz to 13 GHz*

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AUTOMATIC SYSTEM FOR CONTINUOUS MONITORING OF INDOOR AIR QUALITY AND REMOTE DATA TRANSMISSION UNDER SMART_RAD_EN PROJECT

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ABSTRACT. In September 2016, the SMART-RAD-EN Project was launched, funded by the Competitiveness Operational Programme 2014-2020 of Romania, to be developed up to the year 2020. The ambitious overall objective is focus on to the concept of "smart city" in terms of intelligent integrated solutions, which it aims to achieve in international premiere, in order to improve public health by increasing indoor environmental quality and optimizing the energy efficiency of housing in five urban areas of Romania.

In this study, the current status of the development of the prototype system for continuous monitoring and remote data transmission on radon levels and other household air pollutants (CO2, CO, VOCs and temperature, pressure and humidity sensors) is presented, as an important objective in the frame of the SMART_RAD_EN project. The prototype for intelligent monitoring system was assembled and now is involved in the testing process. Metrology and quality assurance of the prototype system will be carried out within accredited European laboratories and by consulting with the international scientific experts. Remote data transmitted will allow: (1) real time interactive visualization, of the impact of user behavior on indoor air quality; (2) information in case of exceeding threshold levels; (3) to produce estimates of future pollution as a result of the correlation with the meteorological parameters (temperature, pressure and humidity) and user activity. The system, metrological validated, will be implemented in 100 houses with high exposure to radon and other ambient pollutants from the main Romanian urban agllomerations – Cluj-Napoca, Bucuresti, Timisoara, Iasi and Sibiu.

Key words: *indoor radon, prototype system, indoor air quality.*

INTRODUCTION

Optimizing the quality of the indoor environment by monitoring and controlling population exposure to radon and other ambient pollutants in homes, reducing associated health risks by implementing preventive and remedial actions represents a global priority (Darby et al., 2006; Field et al., 2006, Council Directive 2013/59/ Euratom; WHO 2009; www.irart.ro; www.smartradon.ro; Cosma and Jurcuţ, 1996; Cosma et al., 2013; Cucoş et al., 2017).

Housing is a very important sector, both from an economic and social perspective, knowing the indoor conditions being a requirement for developing habitat policies. Indoor environmental conditions of housing significantly affect quality of life, manifested by health and intellectual potential, conditions for raising and educating children, safety of daily life and demographic evolution (Pavel et al., 2006).

Indoor air contains a wide range of volatile organic compounds (VOCs) with different chemical and physical properties. Over 900 chemical compounds have been identified in indoor air (Reinhart, 2002). The concentration of these organic compounds depends on many factors (type of activity in the room, ventilation rate, number of occupants, type of furniture, etc.), which makes it extremely difficult to estimate unless they are continuously monitored. Exposure to VOCs has been associated with irritation of mucous membranes (nose, throat or eyes), neurotoxic effects (fatigue, lethargy or headache) or the occurrence of asthma (WHO, 1983). Therefore, monitoring indoor air quality is an extremely important issue and involves the use of precise sensors, able to provide real-time recordings.

Another important factor affecting human health and wellbeing of the occupants of a house is the relative humidity. Studies have pointed out the impact of relative humidity in respiratory infections and allergies (Alsmo and Alsmo, 2014). The relative humidity also affects the rate of formation of formaldehyde, ozone, or salts and acids of sulfur or nitrogen dioxide. In a laboratory study the formaldehyde level tripled by increasing the relative humidity from 30% to 70% (Andersen et al., 1976). In a survey of 20 houses, a good correlation was obtained between the concentration of formaldehyde in homes and the relative humidity (IEC Beak Consultants, 1983). The relative humidity is temperature dependent. As the air temperature raises the relative humidity decreases, with significant variations during the diurnal cycle, or between seasons. Epidemiological studies conducted in this direction recommend maintaining humidity in the range 40-60% to minimize the chances of survival for bacteria and viruses (Alsmo and Alsmo, 2014). Creating a system capable of monitoring temperature and relative humidity and coupling it with ventilation and heating system would maintain moisture in the safe range.

Indoor air quality must be assessed by accurate and representative measurements. Short-term measurements will indicate temporary conditions which are not always representative for long periods of time. Therefore, short-term measurements can lead to false conclusions, reduced performance and unnecessary costs. Therefore, it is recommended the use of systems which allows continuous monitoring, useful both in terms of accuracy and representativeness of results, as well as in establishing the dependency between the monitored factors and occupant activity.

Closely monitoring living conditions and implementing corrective actions where necessary lead, with increased efficiency, to a safe and unmediated improvement of general living parameters, with significant direct and indirect consequences on local and national economic and social development (Pavel et al., 2006).

The present study pointed out the current status of the development of a Intelligent integrated prototype systems with a low energy consumption for indoor air quality in the SMART_RAD_EN project. This prototype have a vast potential to bring considerable gains in terms of health, research, development and technological innovation. Through their uniqueness on a global scale, both the monitoring and remediation systems resulting from the project and the numerical prediction model for radioactive pollution / contamination of indoor air have the potential to generate additional economic value to the research results, the commercial character being intensively supported by introducing radon legislation in Romania from 2018, according to European norms - DIRECTIVE 2013/59/ EURATOM.

MATERIAL AND METHODS

The smart pilot prototype for continuous monitoring and remote transmission of data on radon levels and other household air pollutants, which will be designed and developed in the project, will have the following advantages and SMART features, with a high level of innovation, in relation to the current context:

- The first remote monitoring system of residential radon data, international premiere.
- The first intelligent monitoring system, achieved in international premiere, to associated the radon sensor with other household air pollutants ($CO2$, CO and VOC) and meteorological sensors (temperature, pressure, humidity) relevant to indoor air quality.
- Choosing methods of remote data transmission requiring a minimum cost of operation.
- Coupling the monitoring station to the existing heating and ventilation unit in the house and start / stop them according to the monitored parameters.
- Continuous monitoring of indoor air quality, basic requirement to obtain the certificate of green house.
- Functionality, mobility, autonomy, high efficiency and relatively low production cost, with a total cost of max. 1000 Euro / prototype compared to complex monitoring stations commercially available
- Broad commercial applicability of the prototype. For the production line of over 1000 pieces component costs are reduced by approx. 30%, from which we can infer the economy that cheaper equipment can bring.
- An intelligent eco-friendly system with reduced energy consumption compared to existing devices on the market.
- An intelligent but friendly design, both by its size and by the low level of noise. The aim is to miniaturize the integrated system to have as small an impact on housing.
- The system will function as a mediator between user behavior and indoor air quality.
- Designed as a remote monitoring system will allow: (1) real time interactive visualization of user behavior impact on indoor air quality; (2) delivery of statistically credible data; (3) to inform in case of levels exceeding limit with the possibility to highlight periods of abnormal operating conditions, affecting environmental comfort or health

of residents and thereby to facilitate immediate intervention in case of dangerous accumulation of gases; (4) to produce estimates of future pollution by correlating with meteorological parameters (temperature, pressure, humidity) and behavior.

- The database and server will be as important even after project implementation in that they will provide Romanian and European authorities with relevant indicators on the degree of pollution of indoor environmental quality in connection with energy efficiency in buildings thus providing a bridge between national and international data base.

The proposed monitoring system will include the following hardware and software:

- Sensor for radon;
- Sensors for CO, CO2, VOCs;
- Meteorological sensors for temperature, pressure and humidity;
- Integrated system using on operating system and providing necessary services: analogue and digital data acquisition from the sensors, data transmission via Wi-Fi, local storage of data, implementing control loops and control pumps type actuators, valves;Wireless routers for data transfer via Wi-Fi to a server;
- Server application and web application;
- The client application that allows visualization of data as graphs or tables, setting alarm thresholds and transmitting SMS information with the measurements.

The concentration of radon indoor is influenced by external conditions, such as pressure, temperature, wind strength and direction. For this reason, every city will install an air monitoring station outside.

RESULTS AND DISCUSSIONS

At present, an intelligent device has been developed in the SMART_RAD_EN project that continuously monitors the concentration of the most frequent and dangerous household pollutants (figure 1).

Fig. 1. *The SMART_RAD_EN monitoring system.*

The proposed monitoring system architecture is shown in the figure below.

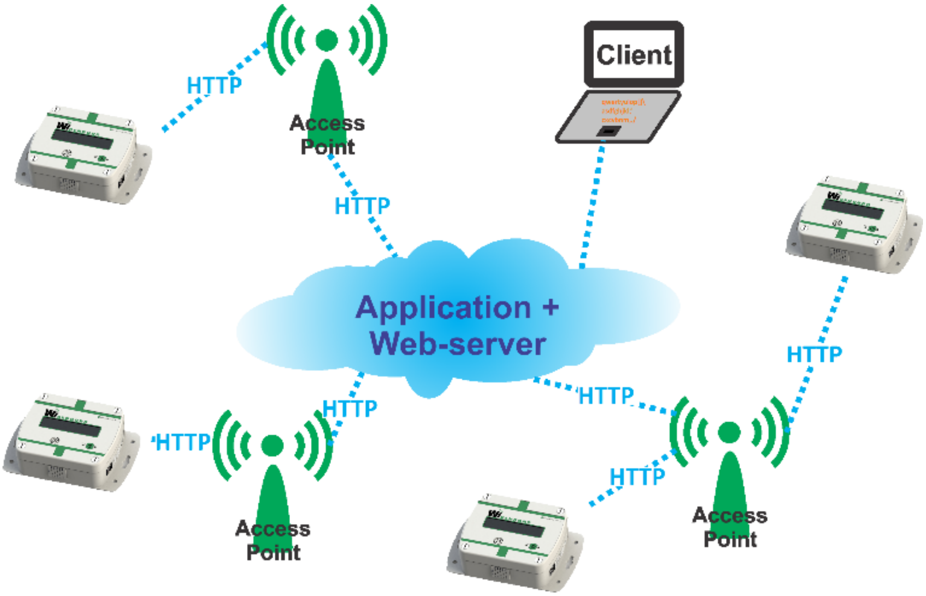

Fig. 2. *The general configuration of the monitoring system.*

The estimated operating principle of the system proposed for development in this project can be briefly presented based on past experience: indoor radon monitoring will be carried out using a Si-PIN photodiode with a size of 100 mm^2, mounted on a fiber glass base, on the surface of which is deposited a thin layer of copper connected to ground. The glass fiber base is placed in a chamber the inner of which is coated with a conductive layer of graphite connected to a positive tension of 250V. Between the copper layer and the conductive layer is formed an electric field that will allow capture and deposition of radon decay progenies. Alpha particles produced by radioactive disintegration of radon and its progenies penetrate the PIN diode and by the energy released and sent to linked electrons, allow the formation of an electrical impulse across the diode. The measurements data can be stored locally or sent using a wireless connection. The software for the device (firmware) will provide support for the used communication protocol to configure device parameters through a serial communication interface, respectively enable radon measurements and remote data transmission to the destination set. Data will be presented to the user using the concept of IoT (Internet of Things).

Environmental conditions influencing diurnal/seasonal variation of residential radon concentration (temperature, humidity and atmospheric pressure) are also measured. In this regard, we will start from the work (Folea and Mois, 2015) describing the authors' contribution to the development of a device for monitoring the ambient environment, a device with low power consumption. This paper presents an integrated device closed into a small box, battery powered, with communication capability via Wi-Fi and which integrates CO_2, temperature, humidity and pressure sensors. Similar devices are commercially available (Six Point ™, 2014 or ENOCEAN Alliance, 2014), but with lower characteristics and a battery running time reduced. To reduce the power consumption of the final device was chosen a nondispersive infrared sensor (NDIR - Nondispersive Infrared) to measure CO_2 with the lowest possible power consumption, available from manufacturers. The developed device, provided with a battery lifetime of up to three years, can measure between 1 and 60 readings per hour. This performance is comparable to most devices with ZigBee® modules, devices consuming less power than Wi-Fi. The device is implemented using PSoC 3 microcontroller 3 (Programmable System-on-Chip) with low power consumption. All sensors integrated into the device have digital interface, providing better measurement precision and simplifying the manufacturing process, in particular by removing the calibration process.

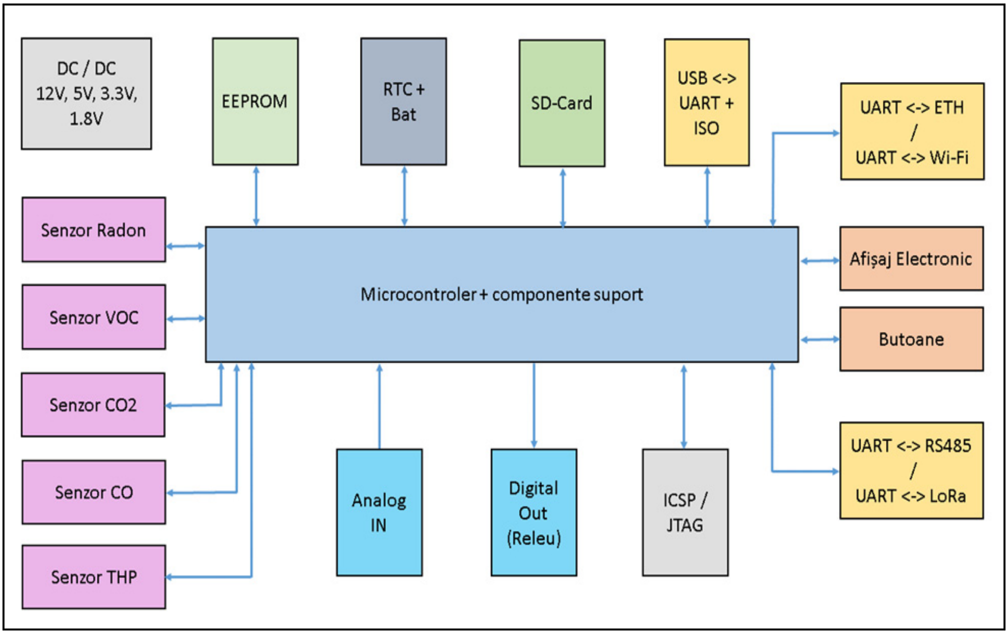

Fig. 3. *The general architecture of the monitoring system.*

The proposed general architecture

The device has as a central element an microcontroller AtMega or AtXMega family from Atmel.Blocks attached to the microcontroller are either sensors or specific blocks whose functionality is described below:

• BLOCK Radon Sensor: is a Tesla TSR2 radon sensor or equivalent that collects the number of specific disintegrations over a certain amount of time. The sensor is interfaced with the microcontroller through a serial port at 3.3V.

• BLOC VOC Sensor: is a volatile MEMS sensor that interferes with the serial port microcontroller at 1.8V.

• BLOC CO2 sensor: is a CDM7160 carbon dioxide sensor, or equivalent, using the NDIR measurement principle. It interferes with a 5V TTL serial port.

• BLOC Sensor CO: is a carbon monoxide sensor of the TGS5141 type or equivalent. The sensor has an analog output, and the internal ADC of the microcontroller is used for measurement.

• BLOC THP sensor: is a sensor or a group of sensors used to measure ambient temperature, humidity and atmospheric pressure. Communication with the microcontroller is done on SPI or I2C depending on the type of sensor / sensors chosen.

• EEPROM BLOCK: is an EEPORM memory used to store the device's set parameters (eg IP server address or SSID credentials for WiFi connection).

• BLOCK RTC + Bat: is the real-time block of the system. The RTC also has a backup battery to keep the time when the unit has a snack. Regular synchronization of the RTC is done online either from the main server or from an NTP.

• SD-Card BLOC: is a block containing an SD-Card that has the role of log memory and where all the results from the sensors as well as the lists with the operating errors are stored.

• USB BLOCK <-> UART + ISO: consists of a UART converter <-> USB (VCP) and galvanic isolation. The USB channel can be used for local device configurations or to download data stored on the SD card.

• UART BLOCK <-> ETH / UART <-> WiFi: is the block through which the device can connect to the internet. Use either a wired or WiFi connection.

• BLOCK Electronic Display: is the display block, state output. It will consist of an LCD or TFT display and some status LEDs.

• BLOCK Buttons: is the input component of the user. It will consist of an On / Off button and a few other menu buttons. The menu buttons can be virtual in the sense that they can be touch buttons if the display is done on a touch-screen TFT.

• UART BLOCK <-> RS485 / UART <-> LoRa: is a block that will be useful to future developments.

The paper presents the main features for each sensor, underlining the important characteristics: measurement range, accuracy, power consumption etc. Each sensor was chosen to have a power consumption as low as possible and meet performance requirements. The measured data are displayed on XivelyTM data server that displays data from sensors connected to the Internet. Upon user's request data can be displayed locally on a backlit LCD. For the CO2 sensor it is also available an automatic calibration option, feature offered by Cozir® manufacturer.

A small number of companies produce integrated SoC solutions (System on Chip) which integrate a radio module for a Wi-Fi network with low power consumption, an analogue interface for sensors and a user programmable processor for which provides a kit software update and support. This paper proposes multi-level software architecture for a monitoring application and provides detailed block diagrams and application components. There are presented various extension cards, such as: an extension to a weather station that includes sensors for temperature, humidity, light intensity and atmospheric pressure; a sensor for density of the particles of dust in the air and an extension with solar cells as an independent source of power for the weather station, as an alternative source of energy. A digital sensor monitoring wind speed and direction was connected to the Wi-Fi device. It was implemented a new firmware to ensure the functioning of the new developed sensor. Several applications were carried into effect, such as: a first application running on a computer and sending data to a server connected via the Internet, this configuration enables wireless sensors to send data to the Pachube database server to be accessed remotely at any time; a second application running on an Android Smartphone and can communicate with the Wi-Fi or the server, allowing, on user's request, local display of sensor data.

CONCLUSIONS

The proposed monitoring system through the new monitored parameters and by its way of rendering the results will act as a mediator between user behavior and indoor air quality. The owner will be able to understand the effects of his household behavior on indoor air quality and will be able in this way to change his routine in order to increase and maintain indoor air quality to the desired level. Creating a smart prototype system for monitoring air quality (radon, CO_2, CO and VOC's) and environmental parameters (pressure, temperature and humidity) will raise a number of challenges:

- Calibration and validation of the results obtained by the sensors included in the monitoring system.
- In situ validation of the results by consulting with international experts.
- Create the conditions through presentations addressed to the economic environment in order to introduce the prototype to production/marketing.

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WASTEWATER QUALITY MONITORING. CASE STUDY: CLUJ-NAPOCA

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ABSTRACT. In Romania, the critical situation of the wastewater treatment plants is caused by the old sewage networks and the purification installations, the modification of the sewage capacity without its adaptation to the constructive parameters, the poor managerial capacity and the poor financial situation of the public utility operators. The wastewater treatment plant from Cluj-Napoca, was recently upgraded, the technology was innovated and introduced the tertiary wastewater treatment stage. This unit collects and treats the wastewater from the city of Cluj-Napoca and from the adjacent areas. To evaluate the quality of the wastewater and of the treated water, the samples were collected over a period of 8 months (September 2015 - April 2016), daily, at the entrance and exit point from the treatment plant. Because our focus was mainly on the tertiary stage, the analyzed parameters were: pH, COD(Cr), BOD_5, total suspensions, ammonium, nitrates, total N, total P. With regard to the quality of the analyzed waters, it can be concluded that all of the eight analyzed parameters show high values in the wastewater and after purification the values decrease, within the maximum permissible limits given by law.

In the months with higher temperatures the quality of the wastewater is weaker, and we noticed that the monitored parameters are slightly higher but also the amount of wastewater increases. On the basis of the results we can say that the efficiency of the purification processes is very good and the tertiary stage introduced in the wastewater treatment process is of high importance especially in the reduction of the phosphorus content.

Key words: *wastewater, treatment plant, chemical parameters, Cluj-Napoca*

INTRODUCTION

This study presents a research regarding the quality of wastewater, from Cluj-Napoca and surrounding areas and the efficiency of the treatment processes and procedures for wastewater treatment, especially tertiary treatment stage.

Wastewater treatment technologies are particularly complex and sophisticated. They use unitary processes of physical, chemical and biological nature. It is a necessity to make a perfect correlation between different parameters of different nature which determines the process of purification.

The advances made today in computer development, dedicated software that appeared, modeling and process simulations have led to the elucidation of many theoretical and practical aspects that were unthinkable two decades ago (Ionescu et al., 2013).

In present, appeared new and modern processes, energy and operational efficient solutions which lead to the achievement of some outstanding performance in wastewater treatment. They can be applied in the rehabilitation of wastewater treatment plants with low implementation costs because they often do not require very large investments. It is desirable to optimize purification processes by using unconventional sources (e.g. the use of the gases from the fermentation process) (Gligor et al., 2010). The correct development of the purification processes is a result of the multidisciplinary activities performed by the operators (Ianculescu et al., 2002).

The chemical composition of household wastewater is greatly influenced by the protein, fat and hydrocarbon content from food, as well as by the composition of water in the feed, which contains carbonates, sulphates, chlorides, iron, etc. within certain limits (Gligor and Blaga, 2009).

The tertiary treatment stage is the finishing treatment that applies after the two steps of the classical purification process and consists of all the processes used for the purpose of removing from the wastewater certain substances called resistant or refractory, which once reached the receivers affects their drinking qualities. For example, the detergents that could not be retained in classical purification promote the appearance of foam at the water's surface of the receptor's, which, besides the unsightly appearance, does not allow the oxygenation of water (Robescu et al., 2011). Also, nitrogen and phosphorus compounds in the primary and secondary trap are retained within 40-50%, once they reach the receptor (especially in storage lakes or in slow flowing water) causing the eutrophication process with unpleasant consequences on water quality. Some researches shows that classical purification processes eliminate up to 50% nitrogen and 40% total phosphorus (Nourmohammadi et al., 2013). Other observations made at various treatment plants in Zurich (Switzerland) have found that the biological process of phosphorus removal (P_{total}) oscillates between 17% and 26%, but in some cases it can result much more inferior yield, as a result of mineralization of organic phosphorus, so that the final effluent contains more dissolved phosphates than the predetermined water (Wuhrman, 1974).

Tertiary treatment stage or advanced water treatment aims to remove the refractory substances from treated water, so that treated water can be reused even in the context of the current water crisis, even for drinking purposes, and the retained impurities to be completely destroyed in order not to affect, in no way, the quality of natural waters (Dima, 2005).

MATERIAL AND METHODS

The wastewater entering in the treatment plant is domestic wastewater, industrial water and rainwater, coming from the city of Cluj-Napoca, Floreşti, Luna, Gilau, Baciu. Total inhabitants served 357141.

The Cluj-Napoca Wastewater Treatment Plant is located on the left bank of the Somesul Mic River downstream of Cluj-Napoca (see figure 1).

The wastewaters in the treatment plant pass through a succession of constructions and installations for cleaning purposes and finally end up in the Someşul Mic River, which is the emissary of the sewerage system of Cluj-Napoca.

To evaluate the quality of the wastewater and of the treated water and to highlight the importance of the tertiary step in the purification process the analyzed parameters were: pH, COD(Cr), BOD_5, total suspensions, ammonium, nitrates, total N, total P.

The samples were collected over a period of 8 months (September 2015 - April 2016), daily, at the entrance (1) and exit (2) point from the treatment plant (figure 1).

The pH measurements were made with a WTW inlab 7310 pH-meter. The pH meter is verified with certified reference materials, calibrated with IL.L.E. – 13. The COD(Cr), BOD_5 parameters were analyzed with volumetric methods, the total suspension with gravimetric method, ammonium, nitrates, total N and total P were determined using spectrophotometric methods (UV/VIS Perkin Elmer Lambda spectrofotometer).

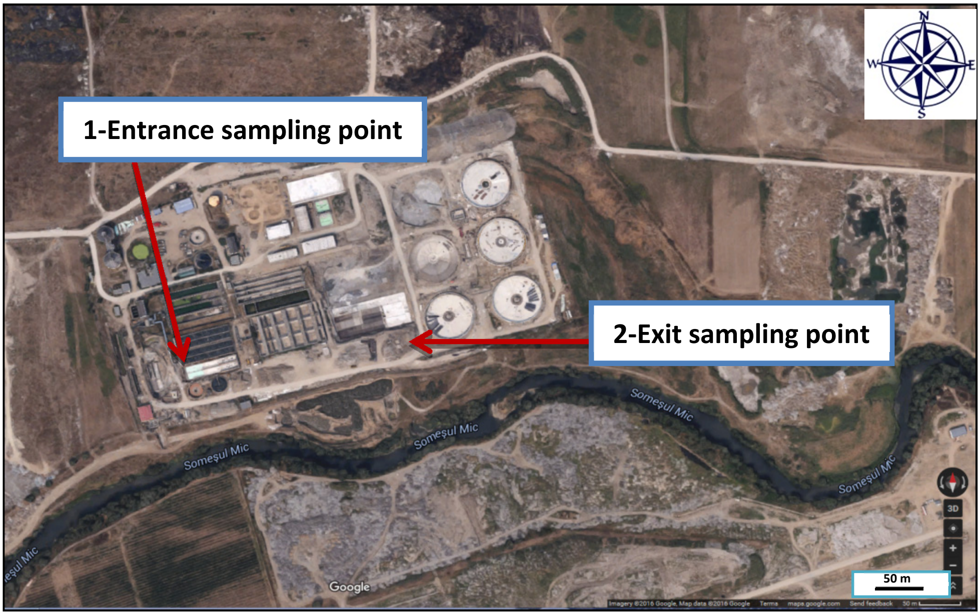


Fig. 1. *Location of sampling points (source: Google maps)*

RESULTS AND DISCUSSIONS

From the obtained results, for each analyzed parameter was calculated monthly averages and these values are shown in table 1 and 2.

Table 1. *Average values for the analyzed parameters from sampling point 1 (entrance - wastewater)*

Month	pH	COD (Cr) mg/l	BOD_5 mg/l	Total susp. mg/l	Ammonium mg/l	Nitrate mg/l	Total N mg/l	Total P mg/l
Sept. 2015	7.66	223.58	99.57	110	27.39	6.1	27.03	3.73
Oct. 2015	7.64	234.79	100.08	111	26.36	4.07	30.95	3.43
Nov. 2015	7.63	230.97	96.95	112	28.22	3.02	31.64	3.73
Dec. 2015	7.62	255.68	121.76	122	30.29	3.53	30.15	3.82
Jan. 2016	7.61	241.72	106.16	110	32.69	3.02	34.02	3.91
Feb. 2016	7.63	244.57	107.33	134	28.31	3.91	33.48	4.63
Mar. 2016	7.66	232.28	100.25	119	29.06	4.1	30.12	3.71
Apr. 2016	7.67	287.95	140.53	144	25.4	4.84	31.27	3.74

Table 2. *Average values for the analyzed parameters from sampling point 2 (exit – treated water), and the MCL (maximum contaminant level according to NTPA-001/2005) for evacuated water*

Month	pH	COD (Cr) mg/l	BOD_5 mg/l	Total susp. mg/l	Ammonium mg/l	Nitrate mg/l	Total N mg/l	Total P mg/l
Sept. 2015	7.57	25.09	2.66	11.12	0.19	15.8	4.43	0.66
Oct. 2015	7.53	18.46	1.54	7.09	0.22	13.4	4.17	0.35
Nov. 2015	7.59	25.98	2.89	14.24	0.2	12.17	4.24	0.44
Dec. 2015	7.6	22.88	1.9	6.55	0.2	12.39	3.58	0.36
Jan. 2016	7.54	20.07	2.67	7.83	0.42	13.55	4.8	0.41
Feb. 2016	7.61	20.63	1.98	5.68	0.41	13.2	4.2	0.45
Mar. 2016	7.58	20.85	2.6	7.5	0.59	13.56	4.56	0.48
Apr. 2016	7.68	29.28	3.77	13.58	0.36	16.54	5.73	0.51
MCL level	**6.5-8.5**	**125**	**25**	**35**	**2**	**25**	**10**	**1**

The pH of the analyzed water samples ranges between 7.5 to 7.7 at both entrance and exit point (see figure 2). In view of this parameter there is no deviation from the legal norms.

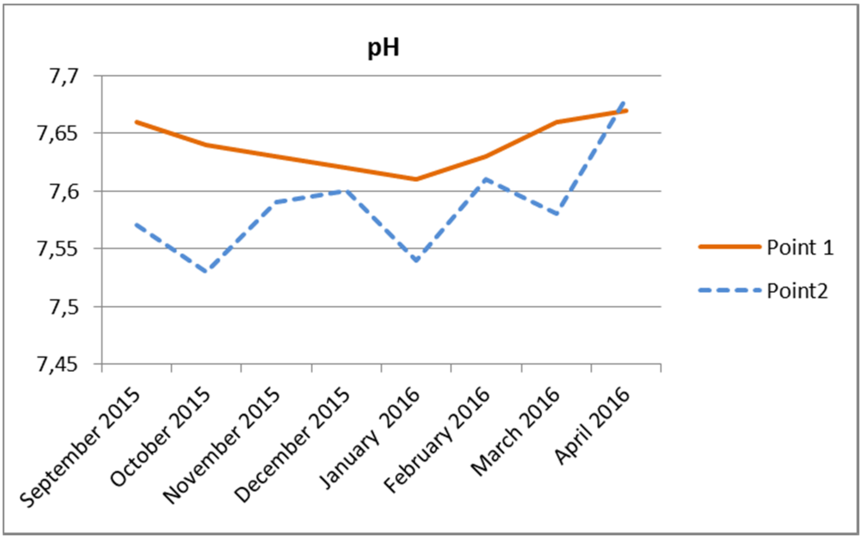
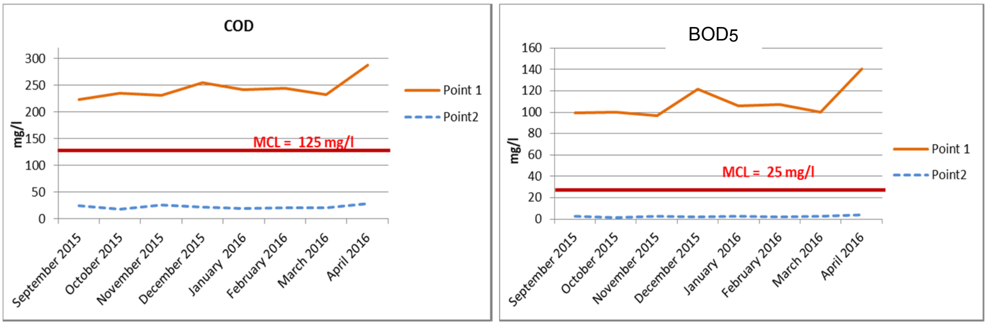


Fig. 2. *Average pH values in the sampling point 1 and 2*

In all the wastewater samples, at each sampling, the content of organic substances is very high, with higher values observed between March and April 2016 due to higher temperatures. The monthly average values for COD(Cr) are between 223 and 287 mg/l. After the treatment of the wastewaters, we observed a significant decrease in the organic substance content, resulting values between 18-29 mg/l (see figure 3a). There is no exceeding of the maximum admissible value (125 mg/l) at the exit point.



a b

Fig. 3. *Average COD and BOD_5 values in the sampling point 1 and 2*

The values of BOD_5 vary similar with those of COD(Cr), with high values at the entry point (ranging between 97 to 141 mg/l) and small values at the discharging point (between 1.5 to 4 mg/l). These low values are due to the consumption of organic matter by the microorganisms responsible for the treatment. There are no exceedings of the maximum contaminant level (25 mg/l) at this parameter at the discharge point (figure 3 b).

The total suspended materials are found in high concentration in wastewater, especially during the periods of snow and periods of heavy rainfall. The salt and sand mixture used in winter contributes to this indicator and during the rain the sewage is "washed", so all the deposits suddenly reach the station. At the sampling point 1 (wastewater), for total suspensions the values range between 110 to 144 mg/l (figure 4).

As a result of mechanical and biological processes, the suspended materials are in small concentrations at the exit point (treated water), with values between 6 and 14 mg/l (under the MCL limit of 35 mg/l given by NTPA 001/2005).

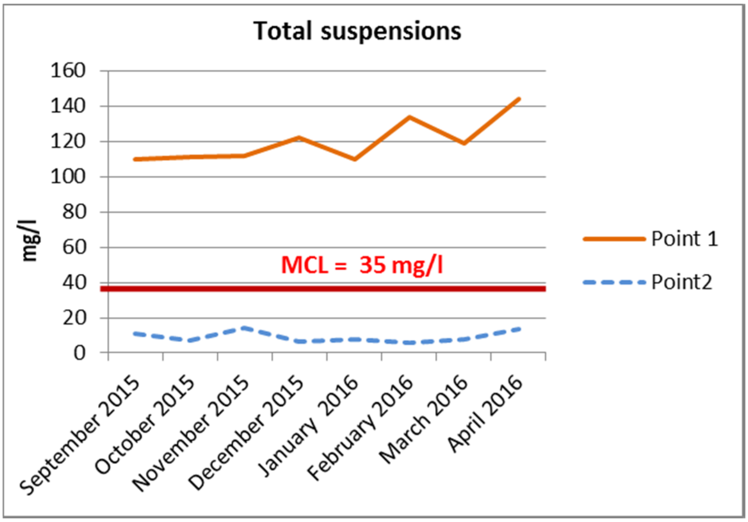
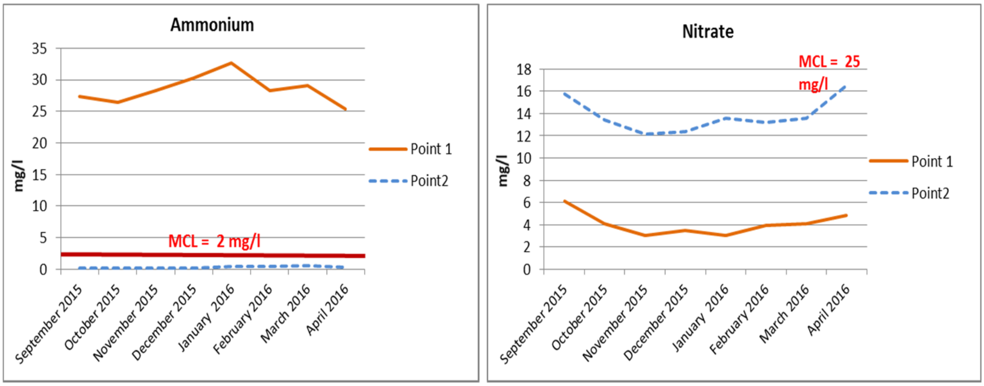


Fig. 4. *Average total suspensions values in the sampling point 1 and 2*

Ammonium values are between 25-33 mg/l at the entrance point, and after nitrification this parameter reach very low values of 0.2-0.6 mg/l at the exit point (under the MCL= 2 mg/l) (figure 5 a).

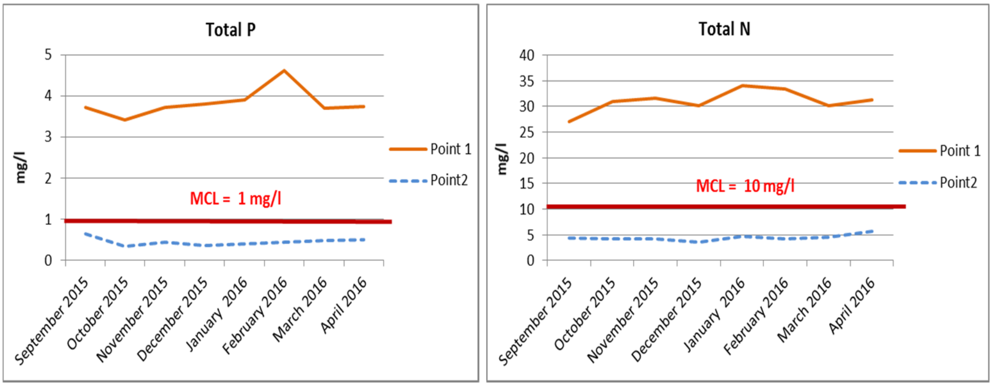
The nitrate concentrations at the entrance point are small, ranging between 3-6 mg/l due to the lack of the chemical industry in Cluj. Following the nitrification and de-nitrification processes, the nitrate concentrations at the exit point, are higher, with values ranging from 12 to17 mg/l, beneath the MCL = 25 mg/l (figure 5 b).



a b

Fig. 5. *Average ammonium and nitrate values in the sampling point 1 and 2*

The concentrations of Total N and Total P decrease significantly after the treatment processes (figure 6a). At the entrance point Total N has values between 27-34 mg/l and after treatment the values drop to 4-6 mg/l, and in the case of Total P, at sampling point 1, the values were between 3-5 mg/l, and drop to 0.3-0.7 mg/l after the biological and chemical processes (figure 6b).



a b

Fig. 6. *Average Total P and N values in the sampling point 1 and 2*

CONCLUSIONS

As a result of the demographic growth and of the uncontrolled discharges of industrial wastewater or chemical pollutants from agriculture, water sources are increasingly contaminated and the amount of wastewater is increasing. Urban and industrial wastewater treatment is a necessity of a constantly developing contemporary society.

In Romania, the critical situation of the treatment plants is generated by the age of the sewage networks and of the purification systems, the modification of the treatment capacity, without its adaptation to the constructive parameters, the poor managerial capacity and the poor financial situation of the public utility operators.

Romania's accession to the European Union has implied and implies the need to solve the problems of environmental protection by modernizing the existing technologies, by creating and putting into operation of some new advanced installations and by providing services adapted to the requirements of the environmental norms.

By assessing the quality of wastewater coming from Cluj-Napoca and from the adjacent localities as well as the treated water quality, it can be concluded that all of the parameters (pH, COD(Cr), BOD_5, Total suspensions, Ammonium, Total N and P) have high values in the wastewater and after its purification the values decreases significant and are within the maximum permissible limits due to the rehabilitation of the station, by modifying its capacity and because of the new introduced technology. In the months with higher temperatures the quality of the wastewater is weaker, we have noticed that the monitored parameters are slightly higher but also the amount of wastewater increases.

On the basis of the results we can say that the efficiency of the purification processes is very good and the tertiary stage introduced in the wastewater treatment process is of high importance especially in the reduction of the phosphorus content.

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