

Temperature programmed desorption mass spectrometry of analcime used as material for soil regeneration

V.A. Pokrovskiy^{1*}, V.M. Bogatyrov¹, N.P. Galagan¹,
N.V. Zaimenko² and V.A. Gavrylov³

¹*O.O. Chuiko Institute of Surface Chemistry, National Academy of
Sciences of Ukraine, Gen. Naumova 17,
Kyiv 03164 Ukraine, ucs@ln.ua;*

²*M.M. Grishko National Botanical Garden,
National Academy of Sciences of Ukraine, Timiryazevska 1,
Kyiv 02014, Ukraine, ivanytskaja@yandex.ru;*

³*Joint Stock Company "Technocrystal", Timiryazevska 1,
Kyiv 02014, Ukraine, office@tecnocrystal.com*

In our preliminary experiments we found out that analcime was the most efficient silicon-containing admixture to organic-mineral fertilizers, improving agro-physical properties of the soil, forming a depot for chemical macro- and microelements, stimulating the root system development, decreasing heavy metals and radio nuclides income to plant organisms. Other silica-based minerals also demonstrated positive effects. Temperature programmed desorption mass spectrometric (TPD MS) and infrared (IR) spectroscopic experiments were conducted in this work to clarify the details of temperature dependent processes occurring in silicon containing minerals, in order to search the correlation between physical and chemical properties on the one hand, and the biological activity of samples under investigation, on the other.

1. INTRODUCTION

Technogenic pressure on agro-ecological systems in Ukraine deforms the natural protective mechanisms of plants, resulting in worsening of agricultural products quality. Our preliminary experiments proved that the application of balanced, granulated and powdered organic-mineral fertilizers of prolonged

activity, based on agricultural and industrial wastes, in the composition with natural silicon containing minerals, brought about positive effects on agro-physical, agrochemical and biological conditions of soils, physiological and biochemical processes in plants and peculiarities of plant development. Such an approach seems to be one of the basic pathways to steady development of biological agriculture.

The research conducted recently proved the significant role of silicon in plant life. Deficiency of this element caused iron and manganese accumulation in plants, sensitivity to fungus and bacterial diseases and decrease of crop capacity.

Since 2001 we have carried out experiments concerning the effects of minerals on agro-physical, agrochemical and biological condition of soils, on physiological and biochemical processes in plants and on peculiarities of plant development. Alancime, aluminium silicate with the empiric formula $\text{NaAl}(\text{Si}_2\text{O}_6)(\text{H}_2\text{O})$ [1], trepel [2], glauconite and other silicon-containing compounds were tested in those experiments.

The following was found:

- analcime improved agro-physical properties of the soil, forming a depot for chemical macro- and microelements, stimulated root system development by 2–3 times, decreased heavy metals and radio nuclides income to plant organisms;
- trepel allowed to save 60% of moisture in the soil;
- glauconite stimulated development of *Azotobacter chroocoeum* tenfold;
- some other silicon containing compounds, for example potassium silica and chlormethylsiloxanes, took part in the formation of organic substance in the soil, decreased soil fatigue, promoted active development of useful microflora, increased mobility of macro- and microelements, stimulated physiological and biochemical processes in plants, increased their adaptive ability to stress factors.

Taking the above into account, it seems reasonable to work out:

- new approaches to modeling optimal level of fertilizer content, including new explanation of experimentally observed paradox, when application of a small dose of fertilizer demonstrated high efficacy due to admixture of small dose of tartaric acid;
- development of small technological lines for production of granulated or powdered organic-mineral fertilizers of prolonged activity on poultry and livestock farms, in enterprises of food industry;
- regulations on application of fertilizers, which would provide for improving soil condition, for controlling purposefully development of plants during the

whole vegetation period, for increasing plant productivity and decreasing soil fatigue;

- well-established database of physical-chemical and biological parameters of Ukrainian soils with the standard models of soil formation dynamics for short- and long-term prognosis of soil quality under the effect of plant vital activity, anthropogenic pressure and climate changes.

The experimental technological line for production of granulated organic-mineral fertilizers has already been built in the Romashky village, the Rokytynskiy region in Ukraine. The large-scale test of produced fertilizers appeared to be efficient, increasing crops productivity and improving soil condition. Tested fertilizers contained poultry excrements, clay and special admixtures, such as cuprum containing compounds and tartaric acid.

Thus, introduction of preparations capable of copper increasing soil fertility, decrease soil fatigue and radionuclide accumulation in crops, as well as stimulate microbiota useful for agriculture, which will allow starting technology of biological agriculture in Ukraine.

Complexity and variety of highly-dispersed natural minerals and their chemical modification by biologically active molecules require application of modern experimental techniques to provide reliable data on composition and structure of mineral-based nanobiocomposites, to make it possible to find the correlation between physicochemical properties and biological activity of synthesized fertilizers, and further optimization of synthesis. TPD MS is one of the promising approaches to this way, particularly in combination with adsorption techniques and temperature dependent IR spectroscopic experiments.

2. EXPERIMENTAL

2.1. Temperature programmed desorption mass spectrometry

(TPD MS) has been developed previously [3-9] for the studies of non-isothermal decomposition of chemically modified high-surface-area ultrafine oxides.

At the moment chemistry and mechanics of nanomaterials are at the initial stage of their formation and development and studies in this line are topical. Among various experimental methods of investigation of nanomaterials the mass spectrometry using temperature programmed desorption is one of the most efficient.

TPD MS is very simple in its basic idea. Similarly to many other methods of solid state physics and chemistry, the sample under investigation is heated by linear law. The temperature increase is to be chosen slow enough to prevent

temperature gradients in the sample. As a rule, the temperature ramp rate is $10^{\circ}\text{C}/\text{min}$ or less.

This scheme allows, first, to identify the products, evolving from the solid sample under the effect of temperature. It also allows following the non-isothermal decomposition of surface complexes in the sample. Mass spectra of individual products are a «fingerprint» of this product. Identification of the volatile product is highly reliable.

A special kind of TPD MS technique has been developed, aimed at studies of adsorption-desorption kinetics and chemical transformations of organic compounds on the surface of ultrafine oxides.

The equipment set included monopole mass analyzer MX-7304A (Ukraine, Sumy, SELMI), liquid nitrogen free vacuum system and magnet-discharge diode vacuum pump NMD 0.16-1 with the pumping speed $0.16\text{ M}^3/\text{L}$, precise thermal regulator with the heating element RIF-101, quartz-molybdenum tube for samples and IBM computer-guided system of registration and monitoring. The resolving power was 2M at 50% of peak height. The energy of ionizing electrons was 70 eV, the residual pressure in the vacuum chamber was no more than 10^{-5} Pa . Linear heating of the sample with a given temperature ramp rate was guided by the programmer RIF-101 with power unit and furnace. The temperature was controlled by the platinum/platinum-rhodium thermocouple installed in the base of furnace and connected with the programmer and the universal volt-ohmmeter B7-21. The sample was located in a quartz tube which was attached to the inlet system of mass spectrometer MX-7304A by special interface. Gas cleaning of mass analyzer was provided by heating of vacuum chamber, inlet system, valves and quartz tube up to high vacuum. Analyzer conditions monitoring and general guidance of the unit were carried out by PC. The equipment parameters obtained in our test experiments are as follows: mass range is 1–400 Dalton, sensitivity is 10^{-8} g ; temperature ramp rate ranges from 0.05 to 30 K/min. The average experiment duration was 1 hour.

Adsorption capacity of ultrafine solids could provide desorption of about 10^{-3} of sample weight. The result was gained in sensitivity of about 10^5 in comparison with the bulk samples. All the experimental scheme of TPD of ultrafine samples became similar to thermal analysis experiment with mass spectrometric monitoring of volatile decomposition products. This similarity has a fundamental base, because surface processes are involved in most of the topochemical reaction models in thermal analysis. On the other hand, typical pictures of thermal decomposition accompanied by multi-channel chemical reactions in adsorption layers were repeatedly observed in our TPD experiments with high-surface-area samples. Products and mechanism of thermal decomposition of surface complexes were identified for organic molecules chemisorbed by the nano-size particle surface. Non-isothermal kinetic parameters, i.e. activation

energy and pre-exponential factors could be derived from the experimental data and the sensible assumptions done concerning transition state structures.

After volatile products of desorption and decomposition had been identified and kinetics of non-isothermal reactions studied, the truth-worthy conclusions could be drawn about the initial surface structure of the sample, the intermediate stages of decomposition and the final result of heating. The pre-exponential factor and activation energy are basic parameters derived from the experiment. Transition state theory is the tool for understanding transition state structure and peculiarities of desorption kinetics. High-surface area materials fit best to this technique. The reason is that, due to high surface area, a lot of species under investigation decompose during the experiment, providing dramatic increase of sensitivity in comparison with the bulk samples. The whole experiment took place in vacuum. The volatile products originating from the sample while temperature increased were analyzed by mass spectrometer. Thermal desorption and decomposition were the products pumped away by the vacuum system, but before being pumped their mass spectra were recorded.

The volatile products of thermal decomposition were treated as follows. The disperse samples each of about 0.1–1 mg weight are placed into a quartz-molybdenum tube and evacuated at 10^{-1} Pa and then attached to the inlet system of a MX-7304A mass spectrometer. The reactor-to-mass spectrometer interface included a high-vacuum valve with an orifice of a diameter 5 mm and the inlet tube of 20-cm length, which was kept at 150 °C. The reaction space was open in the ion-source direction, and at the heating rate used (about 0.1 K s^{-1}) the observed intensity of the ion current was expected to be proportional to the desorption rate, so that diffusion inhibition could be neglected. We assumed quasi-stationary conditions when the shape and position of desorption peaks did not depend on the temperature of the spectrometer interface, the sample dispersion and/or its size. The TPD data would not be considered further if these conditions were not fulfilled.

Thus, the presented TPD MS equipment was aimed at research of ultrafine species and substances. Both equipment management and treatment of experimental data are simple, handy and efficient in work. It seems to be the main advantage of the proposed technique.

As a result of experiment, we obtained about a hundred of thermograms, or about fifty mass spectra. Such a large amount of experimental data is due to high sensitivity of mass spectrometric technique. It allows providing for unequivocal identification of volatile products of thermal decomposition. It allows also presenting reliable interpretation of desorption/decomposition kinetics and the structure of surface complexes in the ultrafine samples.

The advantage of proposed approach was that we have our mathematics in a simple analytical form [7]. We could follow the effect of each parameter and each variable on the experimental data and thus exclude artifacts.

The application of upper technique to mineral powders of analcime, trepel, glauconite and other silicon containing minerals used as a component of organic-mineral compounds, gives the possibility to investigate details of thermal transformations occurring in those minerals under the effect of temperature. In particular, it concerns decomposition of carbonates, and also allows to follow the processes of de- and rehydration and dehydroxylation whose knowledge is important for chemical modification of minerals by organic molecules.

2.2. IR spectroscopy

Measurement of IR spectra of diffuse reflection of the analcime samples was conducted using the FTIR spectrometer "ThermoNicolet". The size fraction of analcime powder, preliminary sieved through the mesh 0.25 mm, was used in experiments. Coarsely dispersed samples were preliminary powdered in the agate mortar. The FTIR spectra of diffuse reflection as the Cubelka-Munk function were treated using the OMNIC program.

3. RESULTS AND DISCUSSION

In the present work the TPD MS experimental approach was used to study evolution of volatile products from minerals under investigation. The results depended upon composition, structure and preliminary treatment of minerals. For example, analcime of various dispersity and origin, demonstrated that the water evolution ($m/z=18$) from the initial samples of analcime in all cases occurred in at least three stages, with the maxima at about 100 °C, 220 °C and 500 °C (See Figures 1, 2).

Existence of one more maximum of water evolution at about 400 °C is also not excluded, but is not obvious. If the origin of a wide diffuse peak between 400 and 600 °C is caused by destruction of surface silanol groups, the assumption of the fourth maximum is not necessary, because dehydroxylation of silica always occurs in wide temperature range in the same temperature interval.

Evolution of carbon dioxide from the sample ($m/z=44$) started for both samples (Figures 1, 2) at about 400 °C and was caused by decomposition of carbonates included in the analcime structure. Comparison of carbonate decomposition in Figures 1 and 2 shows, in the first case, a diffusion delay of evolution process, caused, admittedly, by the diffusion of carbon dioxide in mineral grains. The effect of diffusion delay is much lower for the dispersed sample in Figure 2, which results in peak narrowing and displacement to lower temperature. The result of rehydration of analcime sample is presented in Figure 3.

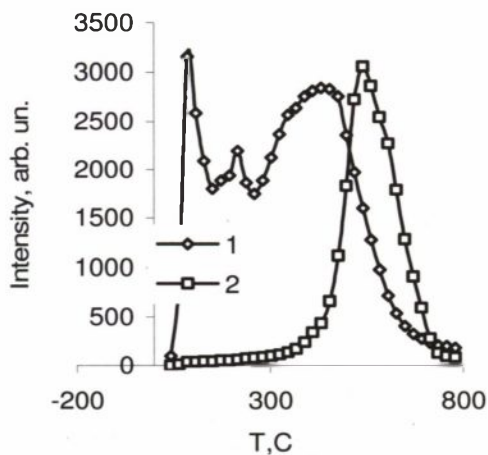


Fig. 1. TPD MS thermograms for two components of mass spectra: H₂O (1); CO₂ (2) for two samples of analcime: #100, industrial dispersion; average particle size 0.5 mm.

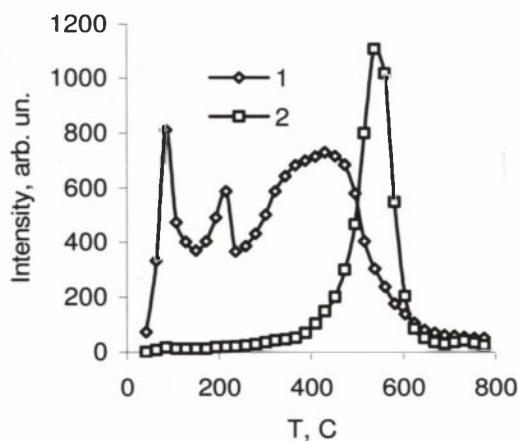


Fig. 2. TPD MS thermograms for two components of mass spectra: H₂O (1); CO₂ (2) for the sample of analcime: #102, special dispersion, average particle size 3 mcm.

As it can be seen in Figure 3, re-hydration after heating up to 800 °C renewed maximum of water evolution at 100 °C with approximately the same intensity as in the initial samples, but other peaks were irreversible. The sharp intense maximum appeared at 300 °C instead of a wide diffuse maximum between 400–700 °C. The maximum of carbon dioxide ($m/z=44$) appeared after re-hydration in atmosphere, displaced to approximately 400 °C. Such a behavior shows that the analcime samples under the effect of temperature undergo deep structural

rearrangements involving water and carbon oxides. The details of those rearrangements need further consideration.

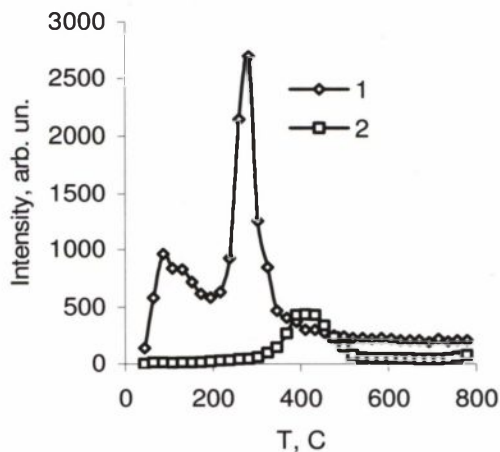


Fig. 3. Two components of mass spectra: H_2O (1); CO_2 (2) after re-hydration of the analcime sample #102. Re-hydration included heating the sample up to 800°C , cooling and further saturation by water vapour.

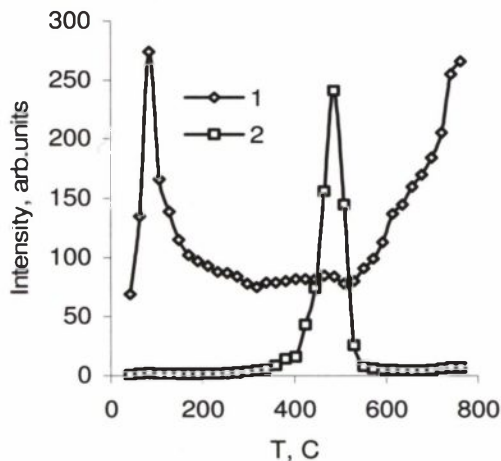


Fig. 4. TPD MS thermograms for the two components of mass spectra: H_2O (1); CO_2 (2) for of trepel. Sample #202; special dispersion up to the average particle size about 20 μm .

In Figure 4 the thermograms of H_2O ($m/z=18$); CO_2 ($m/z=44$) are presented for the trepel sample #202, for comparison with the analcime samples presented in Figures 1 and 2. The peak of carbon dioxide evolution is as narrow as the peak for #102 dispersed analcime sample but was displaced more than by 100°C to

lower temperature. This displacement is probably caused by structural peculiarities of trepel. Water evolution from the trepel sample is similar to physically adsorbed water on the analcime samples. A large peak of water at the temperature higher than 600 °C should be undoubtedly attributed to dehydroxylation of the trepel sample.

The IR spectra for various analcime samples were very much alike. Absorption bands of water and structural hydroxyl groups were observed in the area of valence vibrations at 3700–280 cm^{-1} and deformation vibrations at 1630 cm^{-1} [10].

Significant variations of absorption band intensity in the IR spectra were observed in the area 1430–1490 cm^{-1} , this fact may be connected with the presence of carbonates in the samples under investigation [10]. Taking into account that analcime is a natural mineral, the variation in band intensity with the maximum at 1470 cm^{-1} may be caused by variations of carbonate content in the samples. This assumption was confirmed by mass-spectrometric investigation of the same analcime samples. The presence of CO_2 ($m/z=44$) at the temperature of carbonate thermal decomposition (higher than 500 °C correlates with the absorption intensity in the area of 1430–1490 cm^{-1} in the FTIR spectra.

In Figure 5 the FTIR spectra of analcime are presented, with the extreme values of band intensity with the maximum at 1470 cm^{-1} . For the other studied samples the band intensity is found between those values.

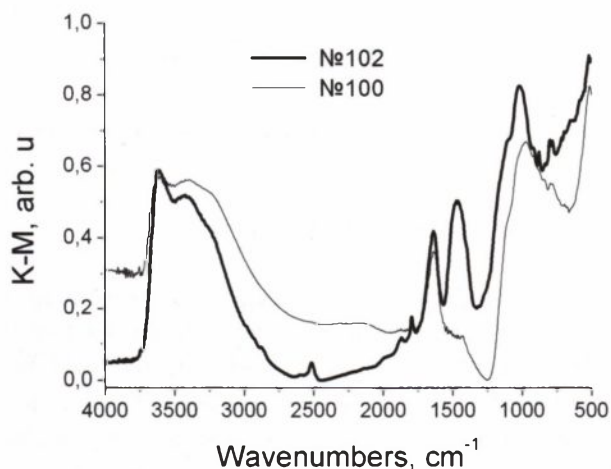


Fig. 5. FTIR spectra of diffuse reflection for analcime. Samples #100 and #102.

In Figure 6 the FTIR spectra of diffuse reflection demonstrate changes obtained in the course of heating the sample from room temperature to 92 °C. The observed changes were characteristic and corresponded to removal of physically adsorbed water from silica adsorbents [11]. As a result of heating from 24 to 92 °C, the change of spectrum of the adsorbed water was observed, including decrease in absorption at the area of valence vibrations (3400 and 3200 cm^{-1}) and decrease in absorption at the area of deformation vibrations at 1630 cm^{-1} . Further heating from 92 to 135 °C did not result in any changes of FTIR spectra. The observed changes in the IR spectra correlate with behaviour of peak $m/z=18$ at 80 °C in the temperature-programmed desorption mass spectra (see Figure 1) thus confirming the kinetics of low-temperature dehydration of analcime.

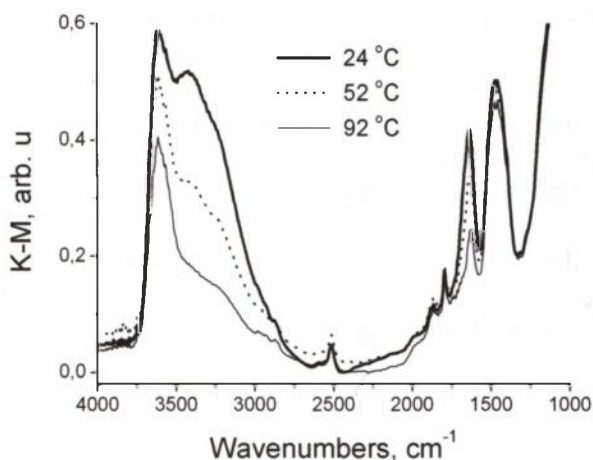


Fig. 6. FTIR spectra of diffuse reflection of analcime at different temperatures. Sample #102.

4. CONCLUSIONS

Analcime of various dispersity and origin, demonstrated that the water evolution in all cases occurred in at least three stages, first of them caused by physically adsorbed water. The origin of a wide diffuse peak between 400 and 600 °C may be explained as a result of analcime dehydroxylation.

Evolution of carbon dioxide from the sample, starting at about 400 °C was caused by decomposition of carbonates included in the analcime structure. The location of observed maximum was caused by diffusion delay of evolution process caused, admittedly, by the diffusion of carbon dioxide in mineral grains.

Re-hydration of analcime after heating up to 800 °C renewed maximum of physically adsorbed water evolution, but other peaks were irreversible. Such a behavior shows that the analcime samples under the effect of temperature undergo deep structural rearrangements involving water and carbon oxides. The observed changes in the IR spectra correlate with behaviour of low-temperature water peak in the temperature-programmed desorption mass spectra thus confirming the kinetics of low-temperature dehydration of analcime.

Water evolution from the trepel sample was similar to that caused by physically adsorbed water on the analcime samples. A peak of water at the temperature higher than 600 °C should be undoubtedly attributed to dehydroxylation of the trepel sample.

The proposed technique opens the way to controlled chemical modification of granulated and powdered minerals by means of temperature programmed reactions. The progress of such reactions, as well as their result, may be controlled by TPD MS in the course of experiment. This possibility is important, taking into account variety in structure and composition of natural silicon containing minerals.

It may be expected that the proposed approach to studies on minerals (analcime in particular) will show the way to explanation of the observed biological effects caused by chemical modification of fertilizers. It concerns, for example, the paradoxical effect of multiple increase of fertilizer activity as a result of additional application of small amounts of dispersed minerals and/or some organic compounds.

Acknowledgement. The authors highly appreciate financial support of the investigation by the Science and Technology Centre of Ukraine (STCU, Project # 3479).

5. REFERENCES

- [1] Public database: <http://webmineral.com/data/Analcime.shtml>
- [2] <http://www.iconcorp.ru/html/trepel.html>
- [3] V. A. Pokrovskiy, *RCM* 9, 588 (1995).
- [4] A. A. Chuiko, G. Ya. Guba, V. A. Pokrovskiy, M. I. Terez, *Colloids Surfaces* 106, 89 (1996).
- [5] V. A. Pokrovskiy *Adsorption Science&Technology*. 14, 5, 301 (1997).
- [6] V. A. Pokrovskiy, R. Lebeda, V. V. Turov, D. Charnas, J. Ryzkowski. *Carbon* 7, 1039 (1998).
- [7] V. A. Pokrovskiy. *J. Therm. Anal. and Calorim.* 62, 407 (2000).
- [8] S. N. Danilchenko, V. M. Bogatyrov, V. A. Pokrovskiy, L. F. Sukhodub, B. Sulkio-Cleff. *Cryst. Res. Technol.* 40, 7, 692 (2005).
- [9] R. Lebeda, B. Charnas, J. Skubiszewska-Zięba, S. Chodorowski, P. Oleszczuk, V. M. Gun'ko, V. A. Pokrovskiy, *J. Colloid Interface Sci.* 284(1), 39 (2005).

- [10] А.В. Киселев, В.И. Лыгин *Инфракрасные спектры поверхностных соединений и адсорбированных веществ*. М.: Наука, 1972. р. 459.
- [11] Накамото К. *Инфракрасные спектры неорганических и координационных соединений*. пер. с англ. М.: Мир, 1966. р. 412.

CURRICULA VITAE



Valeriy A. Pokrovskiy graduated from Taras Shevchenko National University in Kiev, Ukraine with the master degree in Radiophysics and Electronics, 1962. Ph.D. in Chemical Physics, 1974. Doctor of Sciences in Physics of Devices and Technique of Physical Experiment, 1990. Professor in Surface Physics and Chemistry, 2003. Brodskiy award of the National Academy of Sciences of Ukraine for the research cycle “Medicinal chemistry of nanodispersed silica”, 2007. Member of Board of the Ukrainian Chemical Society. Head of the Ukrainian Mass Spectrometry Association. From 1985 till now leading researcher in the Institute of Surface Chemistry, Kiev, National Academy of Sciences of Ukraine.

His scientific achievements include more than 160 peer reviewed publications in application of desorption mass spectrometry to various problems of physical chemistry, chemical physics, surface physics, surface chemistry and environmental protection. Recently his interest is focused on mass spectrometric studies on nanostructured surfaces and supramolecular biologically active systems by various kinds of matrix assisted laser desorption ionization mass spectrometry (MALDI MS).



Natalia V. Zaimenko – agro-chemistry, soil science, plant physiology, ecology. Ph.D. in Biology (1988), Doctor of Biological Sciences (2002). Member of International Society of Space Investigators (COSPAR). Graduated from Ukrainian Agricultural Academy (Faculty of Agro-chemistry and Soil Science). She worked in the National Botanical Garden from 1982 as a junior, senior and leading researcher. Head of Department of Tropical and Subtropical Plants, 1992–1996. Her area of scientific interest are model approaches to construction of artificial biocenoses, including space conditions. She developed fibrous substitutes of soils with regulated physicochemical characteristics and organic-mineral fertilizers of prolonged action, and technological

scheme of their production. She has theoretically substantiated the system of mineral feeding of plants of various ecotypes. The results of research work were published in 150 scientific articles including a monograph, 17 inventor certificates and 10 patents. Starting from January 1, 2005 she is the director of the National Botanical Garden of Ukraine.