Ph.D. Thesis Evaluation Report

Author: Michal Lacko
Title: Studies of reactions of ions with water molecules in the gaseous phase for trace gas analysis.
Reviewer: Mgr. Viktorie Potery, Ph.D.

The thesis describes the major results which were obtained during PhD studies. The conducted research was exploiting several soft chemical ionization mass spectrometry instruments for the detection of trace levels of gasses diluted in the air. The major focus was on the influence of the humidity of the samples on the final products of the ion-chemistry. The significant part of the Ph.D. work was the development of the modelling software which was a complementary tool for the interpretation of experimentally obtained results. The trace gas analysis is widely used in many areas of chemistry. In particular, the measurements of the exact composition of the gas samples can be applied in the environmental and health research.

The thesis is composed of four chapters.

The Introduction chapter is rather extensive. In one subsection the aspects of the ion-molecular reaction kinetics are described in a great detail where the mathematical expressions are also included. The focus was on the chemical ionization and on the influence of the electric field on the reaction dynamics. In the second subsection of Introduction three important analytical instruments which uses ion molecular reaction kinetics for the detection of the trace air components are introduced. The last subsection is devoted to the main goals of the thesis.

In the second chapter author describes the modification of SIFT-MS apparatus with installation of the Gas chromatography unit for pre-separation of the sample. Such a setup allows to detect different isomers and investigate their ionization patterns. The results of the new experimental setup allowed to conduct measurements for several coniferous biological samples where concentrations of several monoterpenes were calculated. The results of measurements were published in scientific journal.

The third chapter is devoted to the description of the computational software KIMI developed by the author. The program is quite complex and thus allows modelling of the ion-molecular chemistry under different experimental conditions. Author showed that results of simulation for the sequence of ion-molecular reactions taking place in SIFT-MS were in excellent agreement with experimental data.

In the last two chapters the author presents major results and conclusions. The output of the Ph.D. work is demonstrated in the attached 6 scientific articles.

Summary

The thesis is scientifically sound. It makes a valuable contribution into a field of mass spectrometry methods, gas-phase ion chemistry and trace gas analysis. The novelty of the results is confirmed by their publication in the impacted scientific journals. Thesis contains the 6 attached scientific articles, 5 of them were already published in the impacted scientific journals.

The work is written clearly and so it is easy to read. The author showed that he successfully mastered the experimental methods and applied them to work with several rather complicated experimental analytical techniques. Author described strong sides of each instrument to solve experimental tasks with the best output. The author showed how secondary reactions which very often complicate analysis of the sample composition can be disentangled from the main chemistry by investigating the influence of type of reagent ion, the collision energy and other parameters on the ion chemistry. Author also showed the ability to incorporate and apply his knowledge of physical chemistry into development of the software for ion chemistry modelling.

Concerning the plagiarism issue, the evaluation software showed low levels of similarities.

Thesis fully satisfies the requirement for obtaining a PhD degree. I give my positive review and recommend the Ph.D. thesis of Michal Lacko, entitled "Studies of reactions of ions with water molecules in the gaseous phase for trace gas analysis" for the defense.

Suggested revisions

Grammar: page 102, last paragraph, "common isomers in investigated", extra "in".
            Page 103, first sentence "VOCs detected the samples" "in" is missing.
            Page 103, last paragraph "The aim of the of the drift" extra "of the".

Content:
- Despite that introduction is quite informative and provides a lot of details concerning the different aspects of ion-molecular kinetics, in some places it could have been shortened in order to focus the reader on the particular parts which were touched or investigated during the Ph.D. work. For example, the negative ions reactivity can be omitted. Shortening the Introduction would also allow extending the Results part which is rather compact in comparison to the previous chapters.
- As I understood that thesis was based on the previously proposed scientific project but since the goals were changed it was not necessary to mention the plans which were not fulfilled since it complicates the comprehension of the real objectives.
- Abbreviation of VOC was not introduced.
- The new developed KIMI software is important part of the Ph. D. work. Unfortunately, the Results section does not contain any graphical output of the software. The Attachment A2 contains pictures where the results of the ion-chemistry modelling are compared to the experimental results. If similar graphs would be added into the thesis as an example of the application of KIMI, the results of the work involving the software would be better represented.

Questions on author
1. How big is sensitivity of gas chromatography technique, could you please compare it to SIFT instrument sensitivity?
2. What are the basic principles of isotopes separation in Gas Chromatography?
3. Could you, please, briefly describe the major properties of the software which you developed, strong and weak sides, what is the main output of the program.
4. The secondary reactions can significantly affect the final ion composition hindering the accurate analysis of the sample. This issue is sufficiently described in the thesis. Could you please comment on the effect of the carrier gas velocity on the rates of the ion-molecular reactions and thus on the possible change of the secondary reactions pathways.

26.09.2022

Opponent   Mgr. Viktorie Potery, Ph.D.