

**WOJSKOWA AKADEMIA TECHNICZNA
im. Jarosława Dąbrowskiego**



ROZPRAWA DOKTORSKA

**Wykorzystanie spektrometrów ruchliwości jonów
do badania procesów jonizacji chemicznej**

mgr Izabela Paulina WOLAŃSKA

Promotor: **dr hab. inż. Jarosław PUTON, prof. WAT**

Promotor pomocniczy: **dr inż. Edyta BUDZYŃSKA**

Warszawa 2025

ABSTRACT

Ion Mobility Spectrometry (IMS) is a subject of ongoing research among both academic experts and teams involved in the development of analytical instrumentation. Current investigations are multifaceted, focusing on phenomena occurring within detectors, including issues related to ion transport and the elucidation of ion–molecule reaction mechanisms. The inspiration for the research presented in this dissertation stemmed from the desire to enhance the understanding of chemical ionization processes in IMS. The primary objectives of this work were to determine the kinetic and thermodynamic parameters of ionization processes and to describe charge transport phenomena under thermodynamic equilibrium conditions in gases.

As part of the doctoral research, experimental studies were conducted on selected organic compounds whose ionization in the spectrometer leads to the formation of either reactant ions or product ions. The initial research direction focused on evaluating the impact of various parameters, such as temperature and humidity, on ionization efficiency, and developing a method for estimating the rate constants of proton transfer reactions. Subsequently, the formation and dissociation processes of ion clusters were analyzed. In particular, the study of cluster formation involving chloride ions enabled the estimation of equilibrium constants and enthalpy values for these processes.

The processes of formation and decomposition of hydrated ions were also studied, allowing for the determination of the reduced mobilities of small ions with a defined degree of hydration. Additionally, the kinetics of electron attachment were studied, leading to the determination of electron capture rate constants for halogenated compounds. These studies of ion cluster formation, stability of ions with varying degrees of hydration, and electron attachment kinetics were based on observations of phenomena occurring in the drift region of the ion mobility spectrometer.

The analysis of the obtained results was supported by a comprehensive literature review, which includes a historical overview of the development of ion mobility spectrometry and its potential applications, with particular emphasis on ion–molecule reaction studies. Key reactions relevant to IMS in both positive and negative ionization modes are described, with a focus on the kinetics and thermodynamics of chemical ionization processes. The dissertation concludes with a summary and conclusions drawn from the conducted research.