

Main Stages of Development and Recent Advances of Mass Spectrometry

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It has been presented the review and analysis of the main evolution stages of one of the most efficient methods for investigation of composition and properties of substances – mass spectrometry. The advantages and application area of the method were described, as well as physical and technical peculiarities of the devices for its realization were considered.

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1. INTRODUCTION

The method for substances investigation, based on measuring the mass of individual elements or compounds, is called mass spectrometry, and the devices for realization of this method are named mass spectrometers. An element in a chemical sense is a substance composed of atoms with a specific nuclear charge (atomic number). The magnitude of this charge determines the location of the element in the Periodic System and its physical and chemical properties, except for nuclear processes. As for the mass number of the nucleus, which is determined by the total number of protons and neutrons in an atom, most elements are not uniform, because they consist of a mixture of several types of atoms, which have although identical nuclear charge but different mass numbers. These atoms are called isotopes. The discovery of isotopy and determination of the masses of the isotopes of certain elements was the result of the first application of mass spectrometry, made by J.J. Thompson in 1907-1910 [1, 2].

The essence of mass spectrometric method is spatial or temporal separation of pre-ionized molecules or atoms that differ by their mass-to-charge ratio (m/z). Such separation is performed under high vacuum by the action of electric and magnetic fields on the ions. Regardless of the method for ion separation by masses, the process of mass spectrometric analysis consists of the following successive operations: 1) conversion of molecules (atoms) of the analyte into the positive ions and the formation of ion beam with different m/z ; 2) separation of the ion beam by m/z ratios in a magnetic or electric field (or a combination) or drifting in space, free of electric and magnetic fields; 3) registration and measurement of each of the components of the ion beam.

Mass spectrometry is one of the most powerful tools to study physical and chemical properties of substances, and mass spectrometer is one of the most advanced and versatile analytical instruments. This is explained by the following characteristic features of this device: it determines the composition of the substance regardless of its physical and chemical properties, provides high

accuracy results of research, allows one to perform analysis in case of the rapid process and very small quantity of a sample.

All mass spectrometric devices are classified according to the method of ion registration. If the ion beams are registered photographically, these devices are called mass spectrographs. Mass spectrum in this case is an image on a photographic plate as a series of lines, each of which corresponds to their m/z value. Recently, mass spectrographs are applied only to accurately measure the masses of nuclei as well as for elemental analysis of solids. Therefore, they are considered to be one of the variants of the mass spectrometer, where the ion currents are registered by electrical methods. According to the principle of operation, mass spectrometers are divided into static (ion separation by masses occurs in magnetic and electric fields, constant in time) and dynamic (ion mass is determined by the time of its passage in the analyzer, or by its period of oscillations in alternating electric and magnetic fields, or by the resonance frequency). In turn, devices for separation and ion beam focusing are divided by functional features into two groups: charged particle analyzers and separators. Using the first, the spectra of ion beam mass or energy are obtained, using the second, it is possible to obtain ion beams, homogeneous by mass or charge, with their subsequent use for ion bombardment of the solid surface to determine the impurities, or, in technological purposes, for the accumulation of the isotope of an element. In this case, powerful ion source with the ion current output of about 10^{-2} A is used.

Modern mass spectrometer is a complex analytical instrument; its construction requires the knowledge in electromagnetic field theory and in ion and electron optics, as well as the achievements of electronics, vacuum, and computer equipment. Despite the fact that to date many different types of mass spectrometers were developed, each of them contains constructive elements whose functions were previous. These are such units as a source of ions, in which the ionization of atoms and molecules of the substance occurs, mass analyzer, in which the separation of ions by mass takes place, and registering system for measuring ion currents and pro-

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cessing mass spectrum. Although the function of these elements of mass spectrometer remained unchanged, their characteristics during the development of mass spectrometry method were continuously improved.

2. ANALYSIS OF LATEST INVESTIGATIONS AND PUBLICATIONS

The last century was a period of rapid development of instruments, methods, and practical applications of mass spectrometric method. In particular, in the 20s F. Aston and A. Dempster made significant changes in the design of mass spectrometric instrumentation at that time. F. Aston positioned the analyzing electric and magnetic fields perpendicular to one another (J. Thompson had parallel ones), which made it possible to focus the ion beam by ion velocity and to increase the accuracy of ion masses determination up to 0.0001 Da at mass spectrograph resolution of 600 [3]. To increase the accuracy of measurement of the relative prevalence of isotopes, A. Dempster used electrical method for detecting ion currents. The separation of ions by masses in his instrument was in a uniform magnetic field with the ion beam deflection angle of 180° [4]. In a short time, F. Aston and A. Dempster have investigated the isotopic composition of 53 elements.

The next stage of development of mass spectrometry was related to the need of studying the structure of atoms, clarifying the nature of nuclear reactions and possibilities of practical use of nuclear energy. In this regard, stricter requirements for accurate determination of isotope mass stimulated the improvement of mass spectrometry equipment, and in the 40s A. Nier, K. Bainbridge, and J. Mattauch created the instruments for measuring the masses of the isotopes with an accuracy $10^{-5} - 10^{-6}$ Da [6, 7]. The experimental results obtained using these devices allowed one to make the table of the exact atomic masses, necessary for the rapid development of theoretical and applied nuclear physics.

Further improvement of mass spectrometric method and apparatus occurred in two areas: improving performance of mass spectrometers with stationary electric and magnetic fields, and development of innovative designs of dynamic mass spectrometers. Success in the first direction was achieved by L. Kerwin and N. Hintenberger, who improved the ion focusing in the mass analyzer due to the position and shape of the magnetic field boundary [7, 8], and by W. Bleakney and J. Hipple, who made the transition to analyzing systems with dual focusing in the combined homogeneous electric and magnetic fields [9].

More accessible, in terms of practical implementation, and very efficient method of improving of mass spectrometric apparatus is the use of mass analyzers with large dispersion. In the devices with a uniform magnetic field the dispersion was increased by enlarging the magnet size or by sloping the magnetic field borders in mass analyzer. The result of using these methods was increased "optical shoulders" of the device and complexity of vacuum system. To build mass spectrometers with a large dispersion, V.M. Kelman et al. applied the magnetic prism with a uniform two-dimensional field [10, 11]. It should be noted that the magnetic prism is an analyzing system that separates

parallel ion beams by masses in the radial plane without their focusing by direction. In combination with electric lenses, two-dimensional magnetic prism allows one to build a device with a spatial focusing that is essential to increase the sensitivity of the mass spectrometer. In the devices with two-dimensional magnetic field the dispersion magnitude does not depend on the size of repelling magnetic field and can be increased by increasing the focal length of the lenses.

One of the promising directions to improve the parameters of magnetic mass spectrometer is the use of axial-symmetric magnetic fields of great non-uniformity, including the fields of heterogeneity factor $n = 1$ or r^{-1} type fields. In the case of a direct boundary such field has the properties of a prism, but by selecting the appropriate position and form for boundary field such focusing can be achieved. For the first time r^{-1} field was used by K. Bainbridge and R. Bender in beta spectroscopy [12]. Later A.F. Malov, V.A. Suzdaliev, and E.P. Fedoseiev have studied the ion-optical properties of focusing magnetic prisms [13, 14], and implemented them in the large separator of charged particles, which had high values of technical parameters [15]. In mass spectrometry, magnetic prism with r^{-1} field was first applied by N.A. Shekhovtsov who built the device with two independent mass analyzers that measured simultaneously two ionic currents at any part of the mass spectrum [16]. High dispersion properties of the magnetic prism were used by U. Matsuda for building the mass spectrograph with dual focusing, and he obtained a record resolution value of 500000 [17].

Ions focusing by the direction in a magnetic field r^{-1} prism was performed by field border form or by additional sector homogeneous magnetic field. However, prism mass analyzers with r^{-1} field have not yet received wide application in serial devices. This is because the ion-optical properties of prism analyzing systems with the magnetic ion focusing by the direction are quite sensitive to small deviations from the target field. As a result, the magnetic field borders have a complex shape, and the field dissipation and accuracy of ion-optical system nodes position significantly affect the analytical parameters of the mass spectrometer. These shortcomings can be avoided if one replaces the magnetic ion focusing with electric one, performed by a lens or lens system located between the ion source and the mass analyzer. Ion-optical system of such devices is not critical to the selection of "optical shoulders" and precise implementation of prism magnetic field [18].

Dynamic mass spectrometers have significantly expanded the capabilities of mass spectrometry method, which explains the importance they have acquired in the second half of the last century. The main positive feature of dynamic systems is the lack of need to focus ions by the direction, that's why technological requirements for precision manufacturing and arrangement of electrodes in dynamical systems are lower than in static ones. Dynamic principles of ion separation allow building the devices with much better individual metrological parameters compared with static systems. For example, top values in the register range of ion masses for time-of-flight mass spectrometer could reach 100000 Da, and the information about the change of environ-

ment can be obtained using such a device in a time less than 10^{-16} sec [19]. Using speed and small dynamic mass spectrometers allowed one to examine a number of physical processes occurring in high and ultra-high vacuum, to explain the behavior of neutral and charged particles in the upper layers of the atmosphere and in outer space, to control the tightness of vacuum and semiconductor products, and to apply dynamic mass spectrometric devices as sensors in automation systems of various technological processes [19-23]. Dynamic mass spectrometers, however, cannot compete with static ones if it is necessary to provide high precision analysis or high resolution.

Along with the development of novel mass spectrometric systems and the improvement of existing ones, the scientists paid great attention to the study on interaction of electrons and ions with molecules, to development of novel ionization methods and techniques of molecular analysis of solids, liquids, and gaseous substances. Apart from mass spectrometers with electron ionization, the devices appear with chemical ionization, photoionization, spark ionization, strong electric field ionization, laser ionization, electrospray ionization, and others. The application area for mass spectrometric methods is increasingly expanding. Mass spectrometers are used in physics, chemistry, biology, geology, technology, and industry for the solving of the following tasks:

- precise measurements of the nuclear masses;
- study of nuclear reactions and the prevalence of isotopes;
- analysis of the chemical composition of the compounds and mixtures;
- studying the kinetics of chemical reactions;
- investigation of ionization processes;
- technological control in nuclear, vacuum, metallurgical, chemical, and other industries.

Expanding the application area of mass spectrometric method in science, technology and industry has set requirements for constant updating of mass spectrometry equipment. And considerable success has been achieved in this direction. The evolution of technical ideas and their implementation in new designs of ion-optical devices provided pioneering achievement for reducing the size of devices, improving their performance and increasing the variety of modifications. Today the park of mass spectrometers in our country has hundreds of devices of different models and cost. Among them up-to-date chromatomass spectrometers,

tandem mass spectrometers, Fourier transform mass spectrometers, mass spectrometric systems using ion cyclotron resonance, and fundamentally new type mass analyzer Orbitrap [24, 25]. In addition to traditional applications, mass spectrometry has come to clinics and medical centers to diagnose diseases and doping control. Without its help it is impossible to perform advanced research in forensic science and ecology because qualitative and quantitative determination of ecotoxins is performed today at femtogram per kilogram of matrix. The main trend of nowadays analytical instruments is an intensive use of microprocessor and computer technology, as well as the building of automated mass spectrometer systems capable of defining of more than 100 compounds per one analysis.

3. CONCLUSION

Despite significant achievements, mass spectrometers are still very complex and costly equipment. Only their high-quality analytical features and versatility of the method encourage consumers to use these devices where high cost pays advantages of this method. The wide application area of mass spectrometers and a variety of solved tasks using them complicate unification of general designs of such devices. Attempts to build several models, able to satisfy a large number of requirements to them, have not led to positive result because of commercial problems. Today mass production of mass spectrometers is established in the USA, England, Germany, France, Russia, and Japan. Recently, Ukraine was also listed among these countries, but for various reasons a few years ago the production was curtailed; hopefully it's temporarily, since its renovation feasibility is obvious.

It should be noted that the success in mass spectrometry have been achieved thanks to the fruitful and hard work of many scientists, engineers, and designers in our country and abroad. In addition to those outstanding individuals who have been mentioned above in brief, it is worth mentioning other researchers and developers of mass spectrometry equipment, who also made significant achievements in the development and application of this method. Among them are J Bernard, V.L. Talroze, N. Volnik, L.N. Gall, A.A. Sysoev, A.T. Lebedev, A.M. Zyakun, V.T. Cherepin, V.A. Pokrovsky, R. Zubarev, and many others. Thanks to them, we have today the opportunity to increase the efficiency of our research and to improve the reliability of its results.

REFERENCES

1. J.J. Thomson, *Phil. Mag.* **13**, 561 (1907).
2. J.J. Thomson, *Phil. Mag.* **13**, 225 (1911).
3. F.V. Aston, *Mass Spectra and Isotopes* (Moscow: Atomizdat: 1948).
4. A.J. Dempster, *Phys. Rev.* **11**, 316 (1918).
5. A.O. Nier, *Rev. Sci. Instrum.* **11**, 212 (1940).
6. K.T. Bainbridge, *Dynamics and Optics of Charged Particles*, in: *Experimental Nuclear Physics*, **1**, 493 (Moscow: Izd-vo Inostr. Lit.: 1955).
7. H. Hintenberger, *Rev. Sci. Instrum.* **20**, 748 (1949).
8. L.F. Kerwin, *Rev. Sci. Instrum.* **21**, 96 (1950).
9. W. Bleakney, J.A. Hipple, *Phys. Rev.* **53**, 521 (1938).
10. V.M. Kelman, L.N. Gall, *Zh. Tekhn. Fiz.* **31** No9, 1083 (1961).
11. V.M. Kelman, L.M. Nazarenko, E.M. Yakushev, *Zh. Tekhn. Fiz.* **42** No5, 830 (1972).
12. K. Zigban, *Alpha-, Beta-, and Gamma-Spectroscopy* (Moscow: Atomizdat: 1969).
13. A.F. Malov, V.A. Suzdalev, E.P. Fedoseev, *Zhn Tekhn. Fiz.* **35** No5, 914 (1965).
14. E.P. Fedoseev, *Zh. Tekhn. Fiz.* **38** No8, 1320 (1968).
15. A.F. Malov, V.A. Suzdalev, E.P. Fedoseev, *Pribery i tekhnika Eksperimentan*, No8, 149 (1969).
16. N.A. Shekhovtsov, V.F. Shkurdoda, A.S. Kuzema, A.S. Koloskov, *Atomnaya Energiya*, No22, 506 (1964).
17. H. Matsuda, S. Fucumoto, M. Nojiri, *Zeitschrift für Naturforschung A* **21** No1, 25 (1966).

18. A.S. Kuzema, O.R. Savin, I.Ya. Chertkov, *Analyzing Systems of Magnetic Mass Spectrometers* (Kiev: Naukova dumka: 1987).
19. V.A. Pavlenko, L.N. Ozerov, A.E. Rafalson, *Zh. Tekh. Fiz.* **38** No4, 64 (1968).
20. J. Barnard, *Modern Mass Spectrometry* (Moscow: Izd-vo Inostr. Lit.: 1957).
21. *Advances in Mass Spectrometry* (Eds. V.L. Talrose and E.L. Frankevich) (Moscow: Izd-vo Inostr. Lit.: 1963).
22. D.G. Beinson, *Mass Spectrometry and its Application in Organic Chemistry* (Moscow: Mir: 1964).
23. A.A. Sysoev, M.S. Chupakhin, *Advances in Mass Spectrometry* (Moscow: Atomizdat: 1977).
24. A.S. Kuzema, A.T. Pilipenko, *Khimiya i Tekhnologiya Vody.* **5** No1, 79 (1983).
25. A.T. Lebedev, *Mass Spectrometry in Organic Chemistry* (Moscow: Binom: 2003).