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Development of mass spectrometers from Thomson and Aston to present

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ABSTRACT

Mass spectrometry contributed to the understanding of the structure of elementary matter including the isotopic nature of the chemical elements, isotopic abundances, nuclear binding, and the investigation of nuclides far-off stability. In this paper the continuous development of mass spectrometers from W. Wien's first mass analysis to J.J. Thomson's discovery of isotopes, F.W. Aston's mass spectrometers, and the Mattauch–Herzog double focusing spectrometer to the present rare isotope facilities will be discussed. Separators with magnetic sector fields e.g. from A.O. Nier and the Oak Ridge separator batteries for large-scale isotope production are included. The first applications to chemistry and geochemistry will be mentioned briefly. The key role of the development of ion optics from the first geometrical calculations towards modern matrix method is addressed. Finally recent developments of mass spectrometers for basic nuclear research including ISOL and in-flight separators for rare-isotope facilities and mass spectrometry with cooled and stored ions will be presented.

1. Introduction

The development of mass spectrometry is closely connected to the early development of nuclear physics starting with the electromagnetic analysis of a gas discharge in a Crookes tube. The Crookes tube is a further development of the Geissler tube, an evacuated glass tube with low gas pressure and two electrodes, a negative cathode and a positive anode to which a high voltage of 10–100 kV is applied. Geissler tubes show a glow discharge and were used for entertainment because of their colorful light effects. The Crookes tube is operated at a much lower vacuum of 0.1 Pascal only, which is the prerequisite for experiments with cathode- and especially anode-rays. Research with the Crookes tube laid the basis for groundbreaking discoveries in atomic and nuclear physics. Best known is the discovery of X-rays by Wilhelm Conrad Röntgen in 1895. Not much later in 1897 Thomson analyzed the deflection of cathode rays in an electric field and determined the mass-to-charge ratio m/e of the electron. He found that the mass of a light particle with negative charge is 1/1800 of that of the hydrogen atom, the lightest known atom. This is the discovery of the electron [56].

Analyzing positive anode rays Wien in 1898 measured the mass of the hydrogen atom. This is the discovery of the proton [61]. He also studied heavier molecules with moderate success because of scattering problems in the bad vacuum. His work can be considered as pioneering for mass spectrometry. Though J.J. Thomson noted that W. Wien was the first to deflect channel rays in a magnetic field the birth of mass spectrometry is the year 1907 with J.J. Thomson's hypothesis that channel rays are beams of charged *particles* with the lighter ones being more deflected than the heavier ones, the principle of mass spectrometry, a revolution in physics. In these times *ether* was used to explain physics. The continuum was the basis of nature. The Greek idea of atoms was not accepted at that time.

On Friday, January 17, 1913 Sir J.J. Thomson gave an address to the Royal Institution: "... in addition there is a line corresponding to an atomic weight 22, which cannot be identified with the line due to any known gas. I thought at first that this line, since its atomic weight is only one-half that of CO_2 must be due to a carbonic acid molecule with a double charge of electricity, and on some of the plates a faint line at 44 could be detected. On passing the gas slowly through tubes immersed in liquid air the line at 44 completely disappeared, while the brightness of the one at 22 was not affected. .... From the relative intensities of the 22 line and the neon line we may conclude that the quantity of the gas giving the 22 line is only a small fraction of neon." This was the discovery of the isotopic nature of the chemical elements, the first positive result of mass spectrometry. Later the same year he gave a lecture to the Royal Society on the same topic [58].

The precision mass measurements started by Aston laid the basis for the Weizsäcker mass formula, a fundamental contribution to the understanding of nuclear binding. Later developments were

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the double-focussing Mattauch–Herzog spectrograph, a design still in use for precision instruments, and the mass spectrograph for high precision mass measurements by H. Ewald. Mass spectrometers were used to measure isotopic abundances. Aston tabulated the isotopic distributions and abundances of the stable elements. Precision measurements of isotopic ratios allow investigating paleotemperatures, age determination of rocks, or the investigation of meteorites for nuclear astrophysics to give some examples of applications. The biggest large-scale application was the Calutron separator batteries for the isotopic separation of the highly fissile ^{235}U for the Manhattan Project.

Today mass separators play a key role in basic physics research for the separation of radioactive nuclei far-off stability. By far largest is the industrial application of mass spectrometers in medicine, chemistry, and process control which is beyond the scope of this contribution. Here we will concentrate on the historical developments of conventional mass spectrometers and mass spectrographs using electric and magnetic sector fields, and their use in physics. It should be mentioned here that the early apparatus were mostly mass spectrographs imaging a full mass spectrum on a photographic plate. Mass spectrometers work with highly sensitive electronic detection methods for the precise measurement of one or more selected masses. Mass separators are used for the separation of rare isotopes. Here all three types will be discussed as they are very closely related. A key role for the development of mass spectrometers plays the development of vacuum, ion sources, and sensitive detection techniques. The development of the design and calculation for mass spectrometers from simple geometric considerations to matrix methods based on fundamental will be touched.

A general historical overview is given in “A History of European Mass Spectrometry”, a collection of papers covering all aspects of the field edited by Jennings [36] and a review by Frantzen [25]. The early history is covered by the contribution of K.S. Sharma to this volume and the books by Aston [10] and by Ewald and Hintenberger [23]. The work of Wien and Aston and the early days of mass spectrometry are covered in papers by Wien [60] and Squires [55]. Separators for radioactive beams are discussed in a review by Geissel [32].

2. Wien and Thomson – the dawn of mass spectrometry

The first experiments in mass spectrometry were made 1898 by Wien [61], later successor of Conrad Röntgen at the University of Würzburg, who studied the nature of the anode rays in a Crookes tube. In an evacuated glass tube with a cathode *A* and anode *a* anode rays were produced (Fig. 1), then collimated when passing the pierced anode. In region *b*, between cathode and anode, the glass tube was shielded from the magnetic dipole field. Between the poles *N, S* of the dipole magnet, inside tube *C*, a homogeneous electric field, not indicated in Fig. 1, was placed so that the field lines were perpendicular to each other. The collimated cathode rays were analyzed in this device, today known as *Wien Filter.* Ions of a velocity v can pass the filter undeflected for a given ratio of the electric field with strength E to the magnetic field with strength B

$$v = \frac{E}{B}$$

The electric and magnetic fields could be adjusted to select a certain velocity. The length of this Wien Filter was only about 5 cm. Wien measured a mass-to-charge ratio of the proton $m/e = 5 \times 10^{-8}$ CGS [61] which is equivalent to 5 10^{-12} kg/C. Today’s value is 5.7×10^{-12} kg/C. He obtained this value only after improving the vacuum connecting a big glass bulb cooled with dry ice to the glass tube to the Wien filter. After the work by E. Rutherford in 1919 Wien’s particle was accepted and named *proton*.

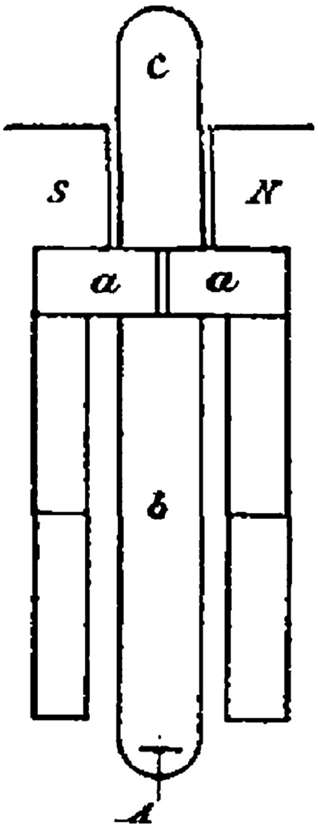

Fig. 1. Wien’s apparatus. The Wien Filter is placed behind the collimator, a thin hole in the cathode plate *a*. The deflection condenser is placed inside the tube *C* between the magnet poles S, N [60].

Wien continued his experiments with heavier ions and laid the basis for mass spectrometry. His results with heavier ions suffered from the bad vacuum through scattering in the residual gas. His attempts to split the canal rays into sharp beams to produce well separated spots at the fluorescent screen failed. The difficulty is to have a sufficiently high pressure in the discharge region *b* to create beams strong enough for observation and to create at the same time low pressure in the observation region *c* to avoid scattering to obtain well separated beam spots.

At about the same time Thomson started his experiments on canal rays at Cambridge. In his first experiments he confirmed the observation of hydrogen. Thomson worked with parallel electric and magnetic fields see Fig. 2 [57]. He separated the discharge region from the observation region by a cathode of about 6 cm length with a bore of only 0.1 mm to 0.5 mm leading to a very fine tube to produce a very thin beam. The positive rays are produced

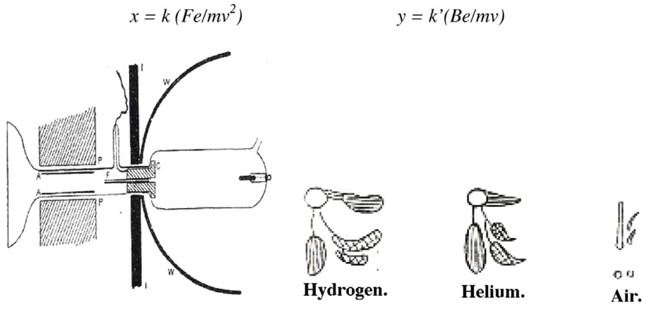

Fig. 2. Left: Thomson’s apparatus with the canal ray production chamber, cathode *C*, the parabola spectrograph with magnetic poles *P,P′* and electric plates *A,A′*, the fine tube collimator *F*, and imaging screen left of the filter. Right: first examples of images for different gases [57].

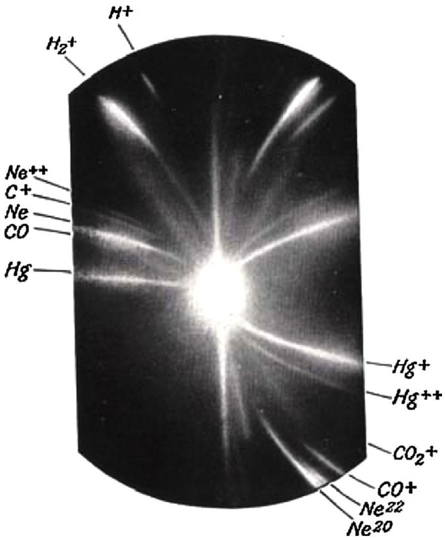

Fig. 3. The famous spectrum from 1913. The three quadrants were illuminated by reversing the electric or magnetic field. In the quadrant lower right the isotopes ^{20}Ne and ^{22}Ne are visible.

in a glass tube by a gas discharge at a voltage of 30–50 kV between anode and cathode *C*. To screen the magnetic field the discharge tube is placed in a soft iron vessel *W*. The gas is introduced by an extremely fine glass capillary. At the very high voltage the cathode rays collect an enormous speed. Those which impinge axially on the capillary leave it as a very fine beam into the highly exhausted analyzing region. First they pass the analyzer of the homogeneous electric field generated between the plates *A,A* placed inside a strong dipole magnet *P,P*. While Wien observed the scintillation of the glass bulb Thomson used fluorescent material, Willemit Zn_2SO_4, which is a large improvement in sensitivity. The length of the parabola spectrograph was only few centimeters. To keep the pressure in the analyzing chamber *G* much lower than that in the discharge tube Thomson used a tube filled with charcoal immersed in liquid air which was an effective absorption pump. The parallel field analyzer creates a two-dimensional spectrum with a horizontal deflection *x* from the electric field of strength *F* and a vertical deflection *y* from the magnetic field *B*

$$x = k\left(\frac{Fe}{mv^2}\right) \qquad y = k'\left(\frac{Be}{mv}\right)$$

A series of parabolas is created, one for each mass over charge with the origin of the undeflected spot. Some of the first images are shown in Fig. 2. Already on the first photo plates Thomson found that the mass parabolas form sharp lines and not blurs. This was the first experimental proof that the atoms of the same element have the same mass within the precision of the measurement. In 1909 Thomson invited F.W. Aston as research assistant. Fig. 3 displays the famous spectrum from 1913 with the two neon lines ^{20}Ne and ^{22}Ne. This is the discovery of the isotopic nature of the chemical elements. To prove this result, Aston tried to separate the two neon isotopes by fractionized distillation without success. Finally he was successful with diffusion through the fine pores of tobacco pipes and obtained two samples with densities 20.15 and 20.28 on the scale of O_2 = 18 [55]. This was the independent proof of the existence of two neon isotopes (Fig. 4).

3. Precision spectrometers with magnetic sector fields: Dempster and Nier

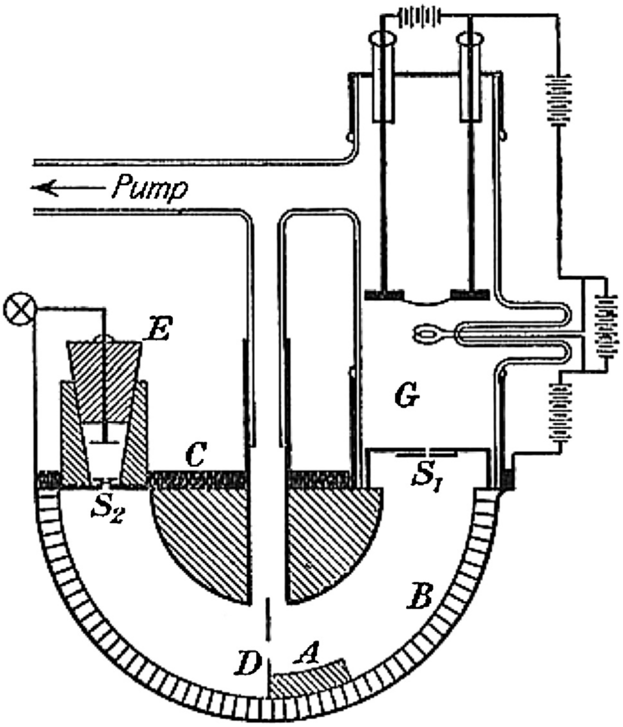

Fig. 4. Dempter's 180° mass spectrograph with ion source *G*, analyzing region *A*, and electrometer *E* [17].

In 1918 Dempster [17] constructed the first focusing magnetic mass spectrometer to separate isotopes. He used a method already applied for the measurement of *e*/*m* of electrons. Ions from the ion source *G* accelerated by a high voltage pass a slit. They follow a half circle in a homogeneous magnetic field in the analyzing chamber *A* then pass a second slit for detection with the electrometer *E*. A general geometric property of ions leaving under small angles moving on circles with the same radius is that their tracks will intersect after 180°. The accelerating potential from 500 V to 1750 V was provided by a battery. Dempster used a thermal ion source. He heated salts on platinum strips or by electron bombardment. By variation of the acceleration voltage, keeping the magnetic field constant, he could measure isotopic distributions and abundances with a resolving power of 100.

In the 1940ies and later magnetic sector field instruments with 90° [34] and 60° sector angles [48,49] were developed. These instruments are compact and have the advantage that ion source and detection system are away from the magnet and magnetic stray fields. Nier's 60° spectrometer (Fig. 5) is the first high-precision spectrometer used for the investigation of isotopic abundances and isotopic ratios with high accuracy. The ions were generated by electron impact on gas or gaseous substances. The high voltage of 1200 V for the acceleration of the ions was generated by a

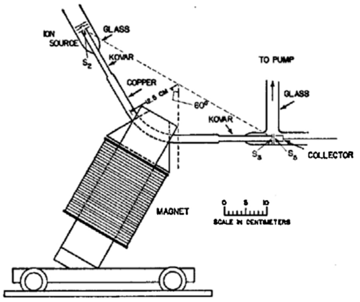

Fig. 5. The Nier 60° sector field spectrometer. The magnetic dipole can be removed for baking the whole system [48].

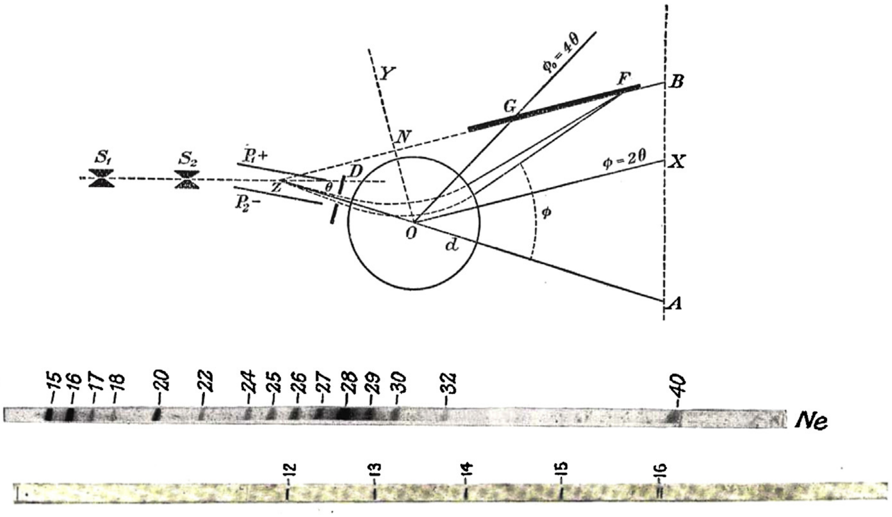

Fig. 6. Upper part: scheme of Aston's first spectrograph [7], middle: spectrum for the neon region taken with the first mass spectrograph [7], bottom: spectrum taken with the second mass spectrograph [8], figure from [10].

stabilized rectifier. The magnet had a low power consumption and could be operated with two 6 V accumulators. The separated ions were measured with an electrometer. The vacuum was generated by a two-stage mercury diffusion pump with a dry ice trap. The whole system could be out gassed by baking. The 60° magnetic sector field spectrometer became a working horse in mass spectrometry. Later improvements for better imaging were: rotating exit and entrance pole angles for vertical focusing and shaping the exit pole. Nier made several significant contributions to geochronology and astrophysics. He developed the uranium-thorium-lead geochronological method to determine the age of the earth, measured isotopic ratios in meteorites, and used stable isotopes as tracers.

4. High-resolution spectrographs: Aston and Mattauch and Herzog

To achieve high resolution the energy spread of the ions from the ion source, mostly a gas discharge, must be compensated. This was first successfully achieved by Aston. In 1919 he built his first mass spectrograph [5] with the aim to focus in velocity the scheme of which is sketched in Fig. 6. The accelerated ions from the gas discharge are collimated by the slit system S_1,S_2, then enter an electric deflector with parallel plates P_1,P_2 where they are deflected by an angle Θ and spread into an energy spectrum which for a fixed mass is a velocity spectrum. A portion of the spectrum is selected by the diaphragm D and passes the magnetic dipole field which deflects in opposite direction by the angle Φ, more than double the deflection Θ in the electric field. The result is a velocity focus F. On a photographic plate along GF a velocity independent mass (m/q) spectrum is obtained. An example for neon is displayed in Fig. 6. The mass resolution is 130 [6]. The result from this and other spectra of that first series was that all atoms had "*masses which are integrally related to a close approximation*". This is the *whole number rule*. Fig. 7 displays a photograph of the first mass spectrograph with the discharge tube *B*, the electromagnet *B* and camera *W*. The pump *G* is a Gaede mercury pump.

Aston was awarded the Nobel Prize in Chemistry 1922 "for his discovery, by means of his mass spectrograph, of isotopes, in a large number of non-radioactive elements, and for his enunciation of the whole-number rule". The whole number rule contributed to a first simple model for the atomic nucleus. The second mass spectrograph [8] was designed to study the deviation of isotopic masses from the whole number rule. It had a cylindrical electric sector field. Fig. 6, bottom, shows a mass spectrum with the mass 16 oxygen-methane doublet ^{16}O-^{14}C^{1}H$_4$. The mass difference reflecting the nuclear binding of the constituents is well resolved. Based on these results Aston plotted this deviation, the packing fraction [8], today we would say nuclear binding, versus the mass number (Fig. 8). This was the basis for Weizsäcker liquid drop mass formula [62]. Aston's third mass spectrograph was finished 1937.

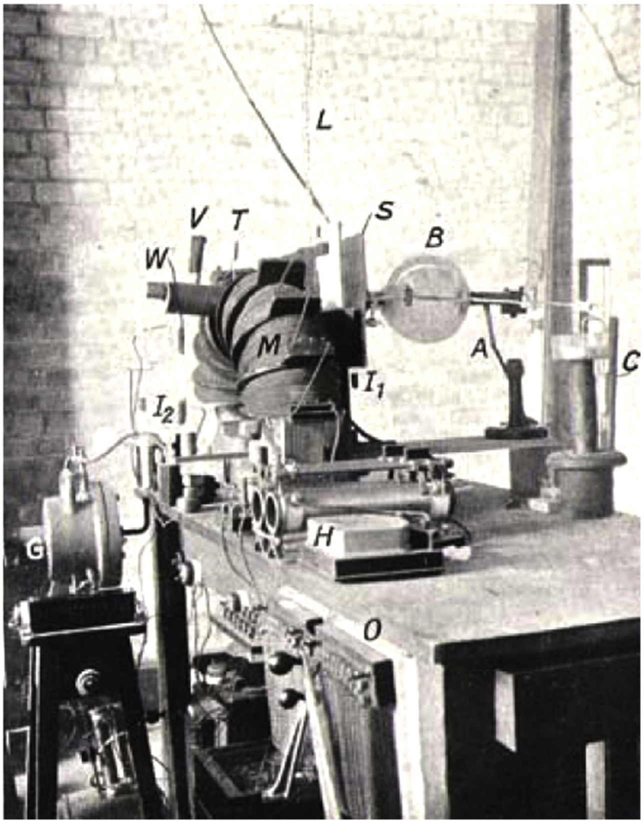

Fig. 7. Aston's first mass spectrograph. Aston's note to the vacuum pump *G* (shortened by the author): "it was set up as shown in 1919 and worked practically daily for 19 years without being dismantled or cleaned throughout the whole time it has been driven by a motor seen below the stool carrying the pump, which. has been made for Scott in his last Polar Expedition".

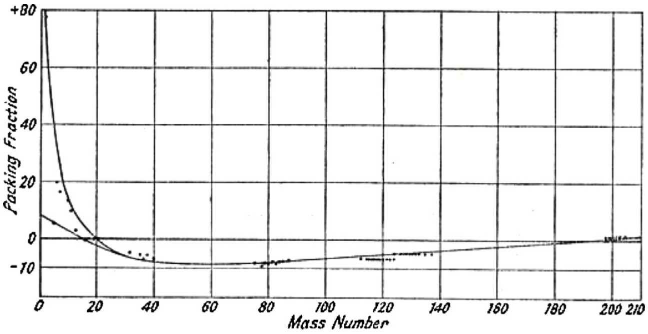

Fig. 8. Aston's packing fraction curve from 1927 [8].

The next progress in spectrometer design is a system which includes energy- and directional focusing called *double focusing*. Bartky and Dempster were the first to calculate a double focusing spectrometer in 1929 [12]. In 1935 Dempster built such a spectrometer in Chicago [18]. In 1936 Bainbridge and Jordan built a double focusing spectrometer at Harvard University [11]. These spectrometers achieved double focusing only for a small mass region.

Mattauch and Herzog developed a complete theory for double focusing spectrometers [42] which achieve double focusing over a large mass region along a full photographic plate (Fig. 9). The figure shows two beams with different velocities, focused in one point at the photographic plate. The spectrometer starts with the entrance slit *S*, followed by an electric sector field. The main parameters are:

$$\Phi = 90^\circ;\ \psi = 45^\circ;\ \Phi_e = -\frac{\pi}{4\sqrt{2}} = 31^\circ 50';\ l'_e = \frac{a_e}{\sqrt{2}}$$

Φ is the deflection angle of the magnetic dipole, Φ_e is the deflection angle of the electric field, ψ is the angle between focal plane *Pl* and the entrance direction of the beam, l_e is the distance from the entrance diaphragm *S* to the electric field, and a_e, and ρ are the radii of the beam trajectories in the electric and magnetic fields. The distance between the sector fields is not fixed as we have parallel beams. The mass resolution of the spectrograph with an average deflection radius of 28 cm in the electric field was about 900.

In the years 1942 to 1944 Ewald built an improved Mattauch–Herzog spectrograph [23,24], the first spectrograph made completely from metal, forged brass, and iron. It was sealed with rubber gaskets (Figs. 10 and 11). To ensure highest resolution special care was taken for precise adjustment and mechanical accuracy. The instrument was hanging in a wooden frame on wires with counterweights to achieve self-adjustment (Fig. 11). The ion source was an anode ray tube (*13* in Fig. 10), separated by a plate insulator from the separator. The precision entrance slit *11* was placed in a chamber with a glass window connected to an oil diffusion pump, followed by the cylindrical plates of the electric sector field with high-voltage feedthroughs *8,8*. A movable intermediate piece *6* sealed with a bellow allows the adjustment between the electric *8,8* and the magnetic *2* sector fields. The cassette with the photographic plate was mounted inside the dipole cassette. This is the only part of the separator which was fixed and connected to the wooden frame. The high voltage was supplied by anode batteries in the upper part of the spectrometer.

With this Mattauch–Herzog type spectrometer a resolution of more than 30 000 was achieved. Fig. 11 displays an image of a mass multiplet at *M* = 15 [23]. For direct mass measurements mass multiplets were created with appropriate chemical compounds. Triplets (Fig. 11) were used for precise measurement of unknown masses. If one knows the masses of a mass doublet, the mass assigned to a third line nearby from the same mutliplet can be determined with high precision [24].

H. Matsuda developed and built double focusing spectrometers of highest resolution. In 1968 he and collaborators measured the atomic mass difference of ^{40}Ca and ^{40}Ar at Osaka University with a resolving power of 700 000 to 1000 000 [27]. He worked on double focusing spectrometers with correction of image aberrations and quadrupole lenses. Among others he calculated a spectrometer with an 85° electric sector and a 72.5° magnetic dipole [43]. The Matsuda configuration is used in Sensitive High Resolution Ion Micro Probe SHRIMP.

5. Applications of sector instruments

Mass spectrographs and mass spectrometers were first applied in basic physics research such as for the investigation of isotopes, isotopic abundances of the natural chemical elements, isotopes from nuclear fission, and high precision mass measurements. Since about 1940 precision measurements of isotopic distributions and ratios were applied for geochronology [46,47], paleontology, and

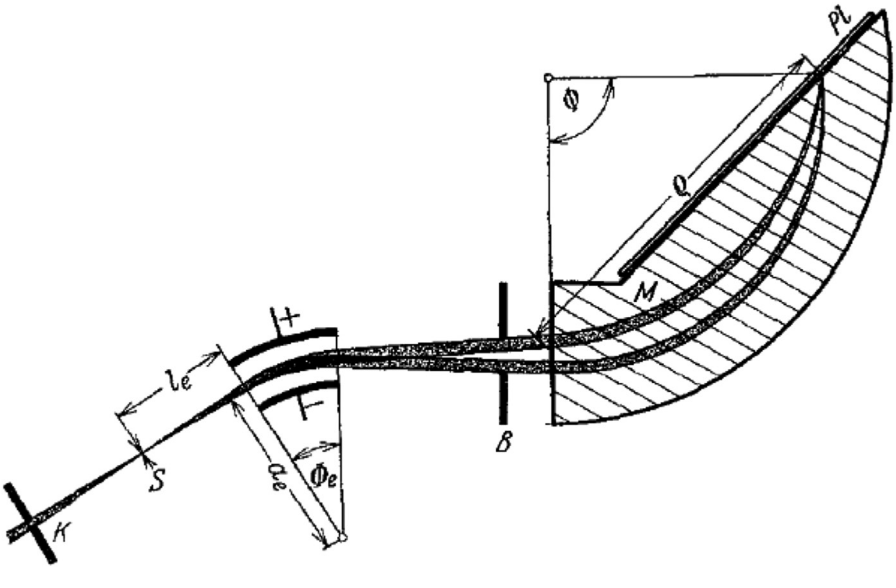

Fig. 9. The Mattauch–Herzog double focussing spectrograph [42].

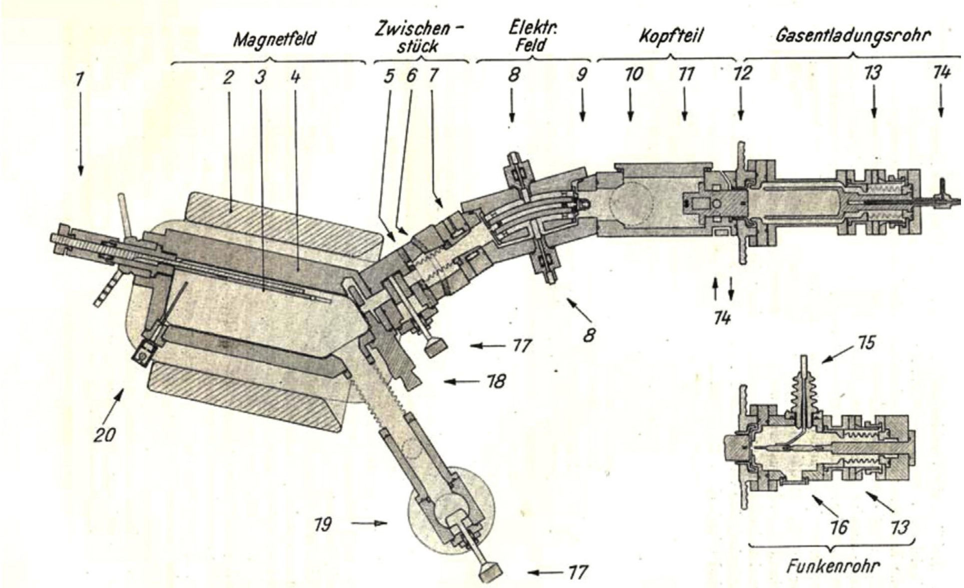

Fig. 10. A new construction of the Mattauch–Herzog spectrograph by Ewald with a resolving power of more than 30 000 [22]. Please note that the beam goes from right to left, inverse to Fig. 9.

the investigation of paleotemperatures (See [59]). Typical methods are the uranium-lead method, used for the determination of the age of the earth, uranium-thorium dating, the potassium-argon, and the rubidium-strontium dating. Paleotemperatures are obtained from $^{18}O/^{16}O$ ratios.

An important application of sector instruments is the separation of stable or radioactive isotopes. A large-scale application was the large Calutron batteries in Oakridge (USA) to separate ^{235}U for the uranium bomb in World War Two. The Y-12 Facility with 1152 Calutrons produced 50 kg of ^{235}U within one year [19]. Due to the shortage of copper, silver for the magnet coils was borrowed from the US treasury. It should be mentioned here the ion optical design is based on Dempster's 180° separator [17].

Since about 1950 Secondary Ion Mass Spectrometry (SIMS) is used to study the composition of materials including rocks and meteorites on the micrometer scale. An example displayed in Fig. 12. The Sensitive High Resolution Ion Micro Probe SHRIMP is a large-diameter double-focussing SIMS produced by Australian Scientific Instruments in Canberra [3], based on the Matsuda spectrometer design [43]. It comprises an 85° cylindrical condenser of deflection radius 1.27 m followed by a 72.5° sector magnet with 1 m deflection radius. The ion beam is created by ion impact sputtering with an ion gun focused on a spot of about 2 μm. The SHRIMP is used for geological and geochemical applications.

The application of mass spectrometers to chemistry started after world war two. In 1948 the first commercial mass spectrometers

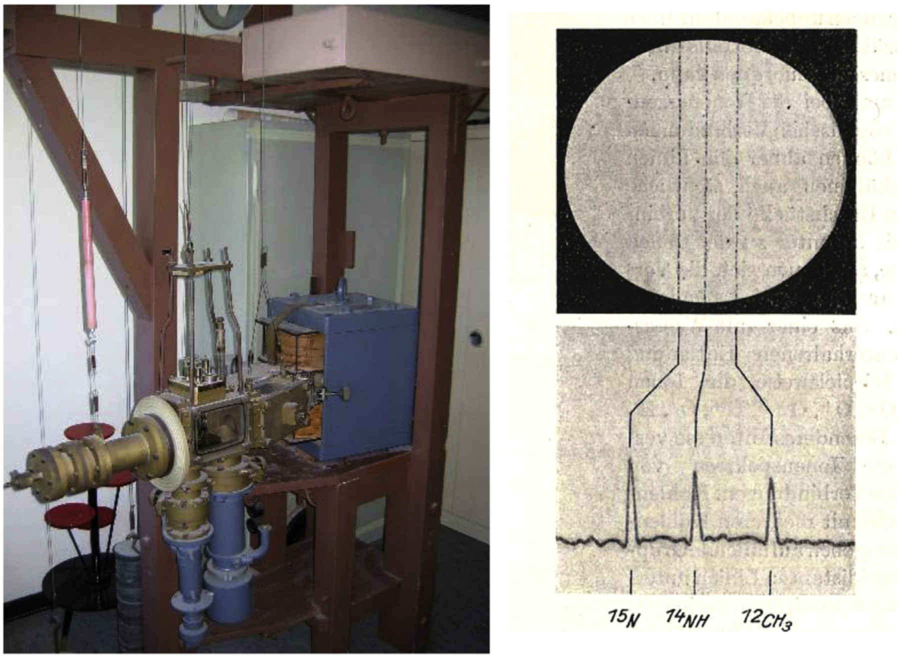

Fig. 11. Left: The Mattauch–Herzog spectrograph built by Ewald, right: triplet of mass 15 [22], upper part: microscopic photograph, magnification 80, lower part: photometric analysis of the photographic picture. The distance between the lines reflects the packing fraction (binding energy).

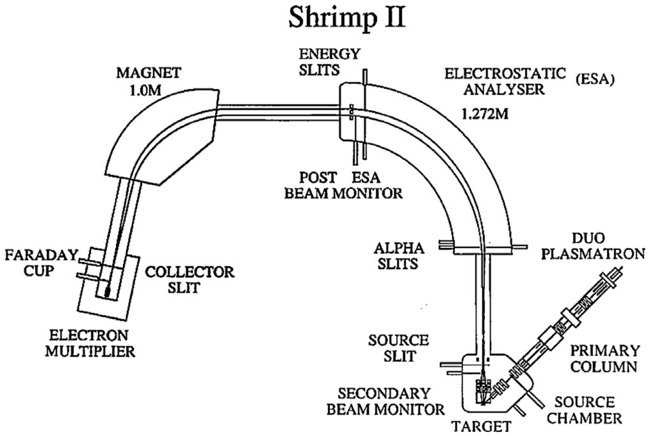

Fig. 12. SHRIMP, a sensitive high resolution microprobe for geochemical application [16]. Courtesy Elsevier.

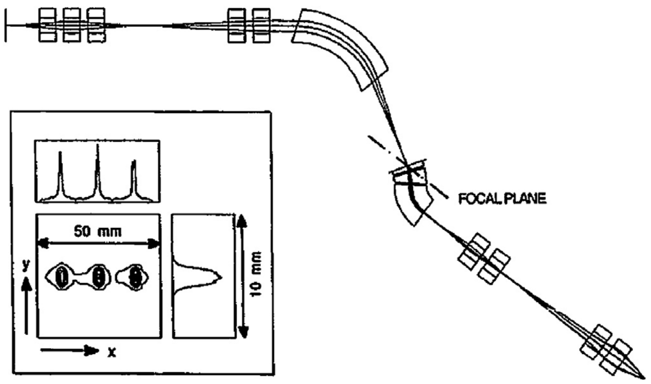

Fig. 13. The General Purpose Separator at CERN ISOLDE with the switchyard at the focal plane and the beam transport to the experiment. The inset displays the spectrum at the focal plane for the isobars with masses 99, 100, 101 and the projected horizontal and vertical intensity distributions [37]. Courtesy Elsevier.

were built by the *Consolidated Engineering Company CEC*, USA and *Metropolitan Vickers Electric Company* MetroVick UK. Mass spectrometry in Germany was started in 1947 in Bremen by R. Jenckel. In 1950 Atlas MAT had the first commercial instrument [25,36].

6. A brief history of ion optics

Already Aston realized that beams of charged particles can be focused like light [5]. The first magnetic focusing has been achieved by Dempster in a 180° spectrometer ([17], see Section 3). Mattauch and Herzog developed a complete theory of double focusing sector instruments [42]. In these papers the ion optical components, electric and magnetic sector fields, were treated as thick lenses and prisms with a momentum, energy, and mass dispersion. The trajectories inside the deflection fields were treated as circles at the intersection with the field boundary continuing as straight lines. In this way focal lengths and dispersions for sector fields including second order image aberrations were calculated with the procedure known from geometrical optics [23].

In 1961 Penner introduced the matrix method to calculate the optical properties of magnetic deflection systems [52]. The equation of motion in magnetic fields is developed as Taylor expansion to higher order and put into matrix form. This method was first set on a solid theoretical basis by Brown [14]. He calculated the matrix elements for magnetic systems. The matrix method was needed primarily for accelerator design. It is convenient, safe, and reliable, and a prerequisite for the calculation of complex configurations. In 1967 H. Wollnik extended the matrix method to electric deflection fields and opened up its application in mass spectrometers (see [63,65]).

The matrix method allows the simple correction of image aberrations including higher orders as well as the application of general rules such as the conservation of beam emittance under conservative forces (Liouville's Theorem), the relation between beam emittance, achievable resolution, and area used in the dispersive field ([64,65]), and the calculation of coupling coefficients which tell the optimum position of optical elements for the correction of image aberrations, to give some examples. For a detailed investigation of the ion optical properties of a spectrometer ray tracing methods have been developed.

7. Sector instruments for rare isotope separation at accelerator facilities

Presently there are a number of types of mass spectrometers available: Radio Frequency Quadrupoles (RFQ), Time-Of-Flight (TOF) and Fourier Transform (FT) and Quadrupole ion traps with a broad field of application in research, environmental studies, and industry. Sector instruments play a minor role [4,36,41].

Today a domain of sector instruments is mass separation of rare isotopes produced at accelerators [32]. The first facility, the Isotope Separator On Line ISOLDE, has been installed in 1967 at the 600 MeV proton beam of the SynchroCyclotron SC at CERN. The intense proton beam is directed on a thick target. Target nuclei hit by the energetic protons disintegrate by spallation or fission to smaller fragments. The reaction products are evaporated from the heated target, ionized and accelerated to the separator. Fig. 13 shows the General Purpose Separator GPS [38]. The seventy degree dipole magnet with inclined field boundaries to achieve vertical focus has a bending radius of 150 cm. Beam focusing includes magnetic quadrupole lenses. The mass resolution is 1000. The beam distribution system at the focal plane can inject into three beam lines.

On-line separation of short lived nuclides was pioneered by the Orsay group [37]. They built a mobile apparatus based on the Nier type spectrometer and investigated short lived sodium isotopes and other alkali nuclides produced by spallation e.g. with the Saturne accelerator at C.E.N. Saclay, France. They also pioneered precision direct mass measurements on unstable isotopes using a Mattauch–Herzog type spectrometer with a spherical electrostatic analyzer. They performed systematic mass measurements of rubidium and caesium isotopes far from stability at CERN ISOLDE. The relative precision was 10^{-6}.

The ISOL method uses thick targets. Reaction products are stopped and evaporated from the heated target which involves target chemistry (see review by Geissel et al. [32]). The *Ion Guide Isotope Separator On-Line* technique IGISOL developed in 1981 at Jyväskylä uses thin targets. The reaction products recoil from the target into an inert gas, typically helium, where they are stopped, extracted by an electric field, and injected into a separator. The IGISOL technique pioneered buffer gas stopping, today the basis of trapping and other applications for radioactive beams produced in nuclear reactions [1].

In-flight separators at heavy-ion accelerators separate nuclides with lifetimes down to microseconds [45]. The first in-flight separators for rare isotopes were gas filled magnetic sector instruments at nuclear reactors. Vacuum separators were pioneered by H. Ewald (see [2]). In 1959 he installed a Mattauch–Herzog instrument for the in-flight separation of fission fragments at the Munich research reactor FRM in Germany [24]. Later the large parabola instrument LOHENGRIN with separated fields based on his idea [50] was built at the research reactor at the Institute Max von Laue–Paul Langevin ILL at Grenoble, France [44]. Modern recoil mass spectrometers

Table 1
Recoil mass separators in operation or under construction.

	Resolving power
CAMEL Legnaro, Italy	280
CARP Osaka, Japan	1000
FMA Argonne, USA	300
HIRA NSC New Delhi, India	240
RMS JAERI, Japan	300
MARA JYFL Jyväskylä, Finnland	250
S^3 Spiral2 GANIL, France	350

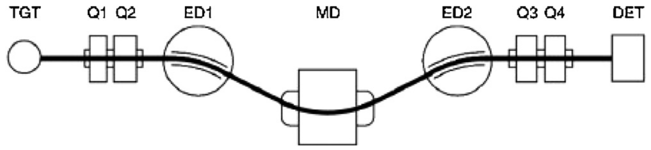

Fig. 14. The FMA at ANL with target area TGT, quadrupole focussing (Q1, Q2, Q3, Q4), two electric sectors ED1 and ED2 and the dipole magnet MD, and the detector area DET [15]. Courtesy C.N. Davids.

(Table 1) are installed at accelerator facilities mostly to investigate fusion products. Examples are CARP at Osaka University (Japan) and FMA at Argonne National Lab. ANL (USA), Fig. 14. They are combinations of one magnetic and one or two electric sectors with quadrupole focussing [32,45].

With in-flight rare isotope facilities of today exotic nuclei are produced by projectile fragmentation or fission in-flight and separated unretarded with their full energy of 100–1000 MeV/A. Special of these new type mass separators is the combination of mass (A) separation with magnetic fields and element (Z) separation by the use of energy loss in an energy degrader. Electrostatic fields are too weak to be used for the deflection of relativistic ions. The first fragment separator is LISE at GANIL [13]. The first dedicated and including the energy degrader ion optically fully calculated instrument is the projectile FRagment Separator FRS at the heavy-ion synchrotron SIS at GSI Darmstadt [29,31]. Fig. 15 displays the scheme of the separator. The projectile beam hits the production target, the projectile fragments are emitted in forward direction into the FRS. The first stage with two magnetic sectors of opposite deflection and four sets of magnetic quadrupole lenses separates in A/Z due to the reaction kinematics as shown in the lower part of the figure for $A/Z=2$. The energy degrader in combination with the second separator stage, mirror symmetric to the first one, separates the single isotope ^{18}F. The FRS is used as isotope separator, high resolving spectrometer, and optionally injects into a beam line system for reaction studies (see contribution of H. Simon to this volume) or experiments in the GSI storage Ring ESR (see contribution by F. Bosch).

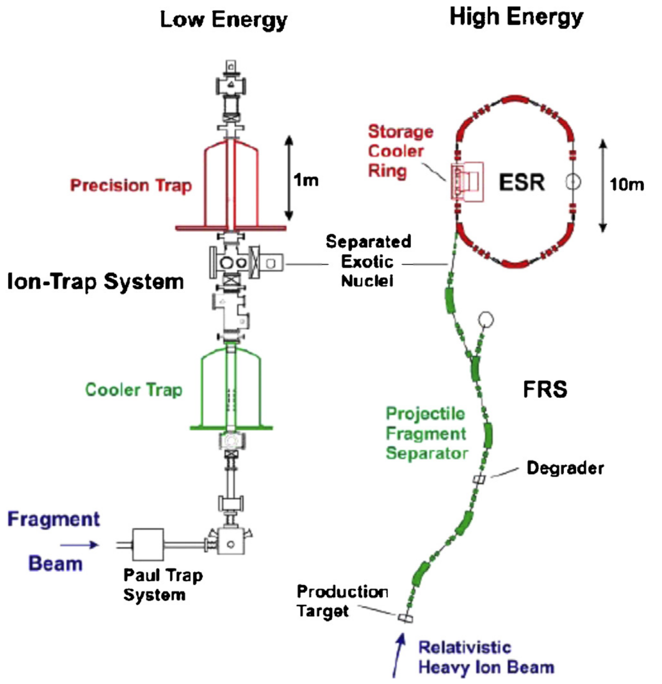

Fig. 16. Left: the ISOLDE ion trap system ISOLTRAP with gas cooling in a cooler trap, right: the GSI FRS-ESR facility, with the ESR equipped with electron cooling. Please note the scale given at the precision trap and at the ESR (from [31]).

Rare isotope separators contributed to the discovery of new isotopes far-off stability and chemical elements. For example, at SHIP and FRS more than 220 new isotopes [53] and six elements were discovered. Discoveries include new decay modes including one- and two-proton decay and boundstate β decay, the doubly magic nuclei ^{100}Sn and ^{78}Ni, superdeformed nuclei, and shape coexistence in nuclei as well as new forms of matter including nuclear skins and halos. With the velocity filter SHIP, the Separator for Heavy-Ion reaction Products at GSI, a further developed version of the Wien Filter with separated fields, six new elements from $Z=107$ to $Z=112$ have been discovered [35]. Facilities operating or under

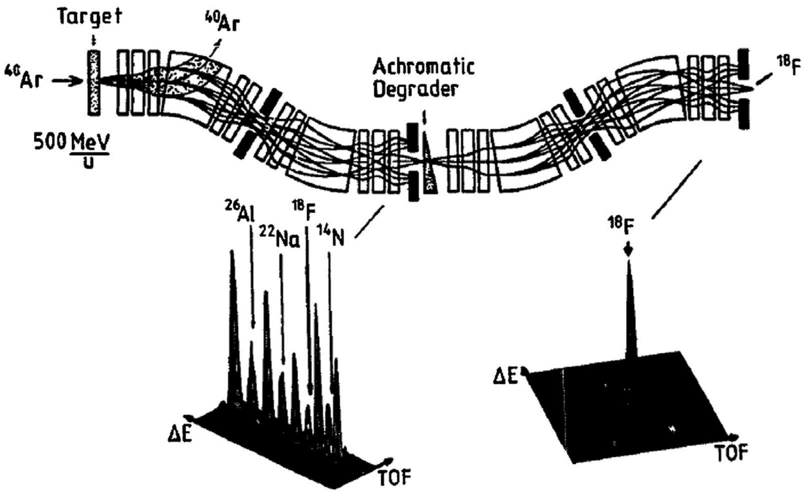

Fig. 15. The FRS. Upper part: ion optical layout with envelops of three different A/Z-beams (first stage) and three different nuclear charges Z (second stage), below: projectile fragments from ^{40}Ar, after first and second selection.

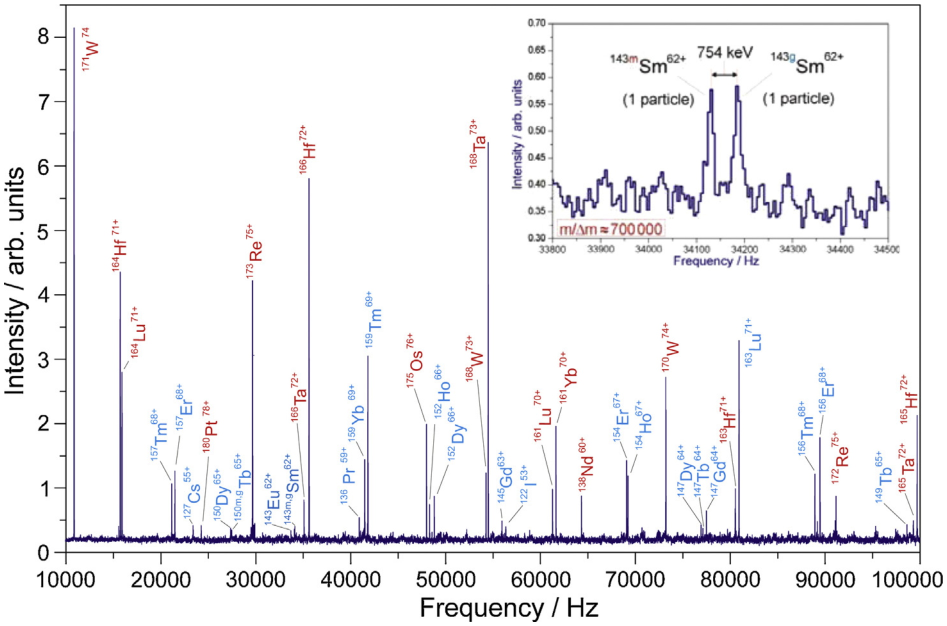

Fig. 17. Portion of a mass spectrum of ^{209}Bi fragments measured in the ESR. The inset shows the well resolved ground- and isomeric states of ^{143}Sm [39].

way are: HIRFL-CSR at Lanzhou (China), RARF at RIKEN (Japan), SPIRAL2 at GANIL (France), HIE-ISOLDE at CERN (Switzerland), FRIB at Michigan State University MSU (USA), and NUSTAR at FAIR (GSI, Germany).

8. Modern mass spectrometry of isotopes off stability: ion traps and storage rings

Around the years 1990–2000 a paradigm change occurred in mass spectrometry [20]: the change from the *(x,p)* phase space in sector instruments to *(E,t)* space in traps (see contribution to this volume by J. Kluge), Radio Frequency Quadrupole (RFQ) spectrometers, and Time-Of-Flight (TOF) systems (see contributions by R.N. Wolf and R.W. Plass). The advantage of time and frequency measurements is a much higher precision of 10^{-6} or higher and sensitivity to single atoms in many cases achieved with cheaper and lighter instruments. An important contribution to these developments is a new technique: ion cooling.

The first TOF spectrometer has been built by Hammer in 1911 [33] for the investigation of canal rays. With the *Mass Synchrometer* developed by Smith atomic masses have been measured by the cyclotron frequencies of ions coasting in a small cyclotron-like magnet system with a very high precision of about 10^7 [54]. MISTRAL, a new construction of this type of RF spectrometer, has been installed at CERN ISOLDE in 1997 by the Orsay group [40]. The first RFQ mass spectrometer was published in 1953 by Paul and Steinwedel [51], the first mass measurement in a Penning trap was performed in Mainz 1978 by G. Gärtner and E. Klempt [28]. The use of ion traps for mass measurements of radioactive nuclei started around 1996 with ISOLTRAP at CERN ISOLDE (First precision mass measurements were already performed in 1990; [21], see contribution of J. Kluge).

Fig. 16 shows two typical examples, ISOLTRAP at CERN ISOLDE (an ion trap with gas cooling connected to the ISOLDE separator) and the ESR system at GSI connected to the FRS. The ESR stores and cools ions at relativistic energies. It is coupled to the projectile fragment separator FRS ([26], F. Bosch, contribution to this volume). The ESR is well suited for large-scale inspections of the nuclear mass surface. The first mass measurement with stored and cooled fragments was performed in 1992 [30]. In the fragmentation of ^{209}Bi more than 500 masses including more than 200 new masses were measured and evaluated [39]. The resolving power is 2×10^6 (Fig. 17).

9. Concluding remarks

Hundred years of mass spectrometry and hundred years of nuclear physics, a fascinating story beginning with resolving two neon isotopes, revealing the isotopic nature of matter, the measurement of nuclear binding, and today looking into the details of nuclear structure of unstable nuclei. The improvement of the resolving power of the spectrometers is closely related to increasing insight in the structure of the atomic nucleus. History shows the huge progress in the investigation and understanding of the properties and nature of elementary matter. Mass spectrometry has been developed from instruments in the laboratory to large-scale application, from basic research to industry, an excellent example how developments in basic research contribute to industrial application and frontline research.

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