

AN EVALUATION OF A MASS SPECTROGRAPH

by

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## INTRODUCTION

The discovery of the presence of several isotopes of Neon by J. J. Thomson in 1913 introduced the mass spectroscopy as an analytical tool. Today, because of the variety of applications, the mass spectroscopy has become a well-established research and industrial instrument. The numerous fields of mass spectroscopy (Inghram, 5; Kerwin, 7), including the rapid analysis of chemical mixtures, the quantity separation of isotopes, and the determination of the presence of isotopes, their masses, and their relative abundances, have caused the specialization of the instrument through modifications of one or more of the three major components.

These components (the source for producing the beam of ions, the analyzer for resolving the beam into a mass spectrum, and the detector<sup>1</sup> for recording the resolved beam) are so designed as to meet particular requirements. For instance, in accurate mass determination, a high resolving power is required as afforded in a double-focusing spectrograph. In the study of surface phenomena, the surface under investigation may be used as a source. Consequently, a secondary ion source may be designed. And in analyzing fast reactions, a detection system with a rapid panoramic scanner is required.

The mass spectroscopy discussed in this paper was designed by Lewis and Hayden (9) and constructed by More (10) and Hartke (3).

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<sup>1</sup> The mass spectroscopy is any mass analyzing instrument employing the major components of source, analyzer, and detector; the mass spectrograph is a spectroscopy whose detector is a photographic plate; the mass spectrometer is a spectroscopy whose detector is some sensitive electrical device.

The instrument is a spectrograph with a 60° magnetic analyzer and a hot anode source. It was built, as explained by More<sup>1</sup>, as a small quantity separator of radioactive materials and for isotope analysis in the rare-earth region.

The purpose of the research reported here was to evaluate the instrument in terms of the purposes for which it was constructed and to make improvements in the instrument wherever possible without making radical changes in the source, analyzer, or detector.

## GENERAL DISCUSSION OF THE MASS SPECTROGRAPH

### Theory of the Mass Spectrograph

Charged particles of the same energy or velocity, but differing in mass or charge, are acted upon by forces of different magnitudes under the action of a magnetic field. This principle is the basis of mass spectroscopy.

The force exerted upon a single particle of mass  $m$  (gms) and of charge  $e$  (coulombs) in a magnetic field of strength  $B$  (gauss) is represented by the vector equation:

$$\vec{F} = \frac{e\vec{v} \times \vec{B}}{10} = \frac{d}{dt} (m\vec{v}) \quad (1)$$

Most frequently the ion is made to move at right angles to the magnetic field. The velocity of the particle is then given in scalar form by:

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<sup>1</sup> Frequent reference will be made to the theses of More (10) and of Hartke (3) on the construction of the mass spectrograph. Thus, when reference is made hereafter, only their names will be given.



$$F = \frac{Bev}{10} = \frac{mv^2}{r} \quad (2)$$

where  $r$  is the radius of curvature (cms).

An electrostatic field is used to accelerate the ions, directing the particles into the magnetic field with a kinetic energy given by:

$$KE = \frac{1}{2}mv^2 = eV \times 10^9 \quad (3)$$

Here  $V$  is the accelerating potential in volts.

From equations (2) and (3), the electronic charge ( $e = 1.60 \times 10^{-19}$  coulombs), and the relation  $m = A/N_0$ , where  $A$  is the atomic weight and  $N_0$  is Avogadro's number ( $N_0 = 6.025 \times 10^{23}$ ) the equation for the radius of curvature for singly charged particles becomes:

$$r = \frac{144}{B} \sqrt{AV} \quad (4)$$

### Magnetic Focusing

Plate I shows two trajectories of ion beams, each homogeneous in energy and mass. Because of the finite width of the slits of the ion source, these beams are divergent as they enter the magnetic analyzer. The focusing action of the analyzing field refocuses the divergent beams, a process known as direction focusing or single focusing.

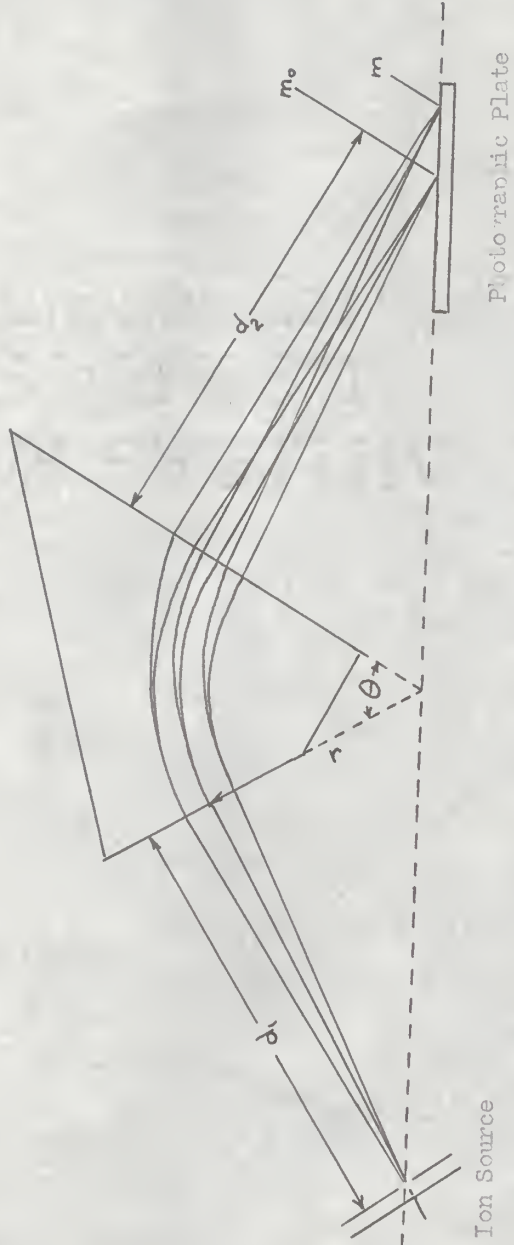
In analogy with optics, an equation for the focusing action of the magnetic analyzer, for normal entry and exit, can be given as:

$$(d_1 - g) (d_2 - g) = f^2 \quad (5)$$

EXPLANATION OF PLATE I

Diagram of  $\theta$ -sector magnetic analyzer showing two divergent ion beams, each homogeneous in mass (masses  $m_0$  and  $m$ ) and energy.

PLATE I



where:

$$f = r \csc \theta ; \quad g = r \cot \theta \quad (6)$$

The quantities  $d_1$ ,  $d_2$ , and  $f$  are the object distance, image distance, and focal length, respectively, for the magnetic prism.  $\theta$  is the angle through which the beam is deviated. A more general treatment has been given by Herzog (4).

For  $d_1 = d_2$ , a symmetrical type analyzer, and for an ion deflection of  $60^\circ$ :

$$d_1 = d_2 = 1.732 r \quad (7)$$

#### The Hot Anode Source

The simplest and most common hot anode source consists of a tungsten ribbon coated with the elements to be analyzed. When the filament is heated, some of the material is evaporated as ions through electron affinity of the filament (Inghram, 5). This surface ionization source is best suited for analyzing elements with ionization potentials below the work function of the hot surface.

Ionization efficiencies for positive ion formation are usually low, an optimistic estimate being 15 per cent (Lewis and Hayden, 9). From measurements of the radioactivity of the source and the image formed on a photographic plate, transmission of these ions through a spectrograph has been estimated to be about 10 per cent.

Methods for the deposition of rare-earths onto the filament has been discussed by Aston (1) and Inghram, et al. (6). Inghram (5) listed the elements, mainly the alkaline earths and the rare earths, which have been successfully used for positive ion



emission. Ionization efficiencies for negative ions are usually very low.

### Photographic Detection

Developable latent images are formed by the charged particles on films sensitized to the ultraviolet region. It has been reported (Lewis and Hayden, 9) that for a developable image,  $10^{10}$  ions/mm<sup>2</sup> must strike the photographic plate.

Unless mass assignments can be made through identification of known lines, a method of marking the photographic plate must be employed. As an example, one such method of marking has been discussed by Bainbridge and Jordan (2) in which the fiducial mark was an image formed by focusing a beam of light on the photographic plate through an opening in the plate holder.

### Resolving Power

The limit of resolution is defined as the ratio  $\Delta M/M$  where  $\Delta M$  is the difference in mass of two ions whose images are just completely resolved, and where  $M$  is the mean mass of the ions. The resolving power is the inverse of the limit of resolution.

From equation (4) the theoretical limit of resolution can be expressed as:

$$\frac{\Delta M}{M} = \frac{2\Delta r}{r} \quad (8)$$

The energy dispersion of the ions,  $\Delta V/V$  is considered negligible compared to  $2\Delta r/r$  (Inghram, 5).

For single focusing analyzers, the resolving power is usually 250 or less (Kerwin, 7). A resolving power of 500, however, has been reported for the instrument designed by Lewis and Hayden (9).

## EXPERIMENTAL TECHNIQUES

### The Ion Source

Experimental difficulties were numerous, mainly centering about the ion source assembly. The source assembly lacked rigidity. Removal of the source holder from the instrument usually implied construction of an entirely new assembly. Previous to the construction of a more rigid source holder, the box type holder described by More was observed in an evacuated glass chamber. The nichrome leads expanded appreciably and the tungsten filament showed considerable distortion. This accounted for the frequent shorting of the filament against the collimating slit during operation of the spectrograph.

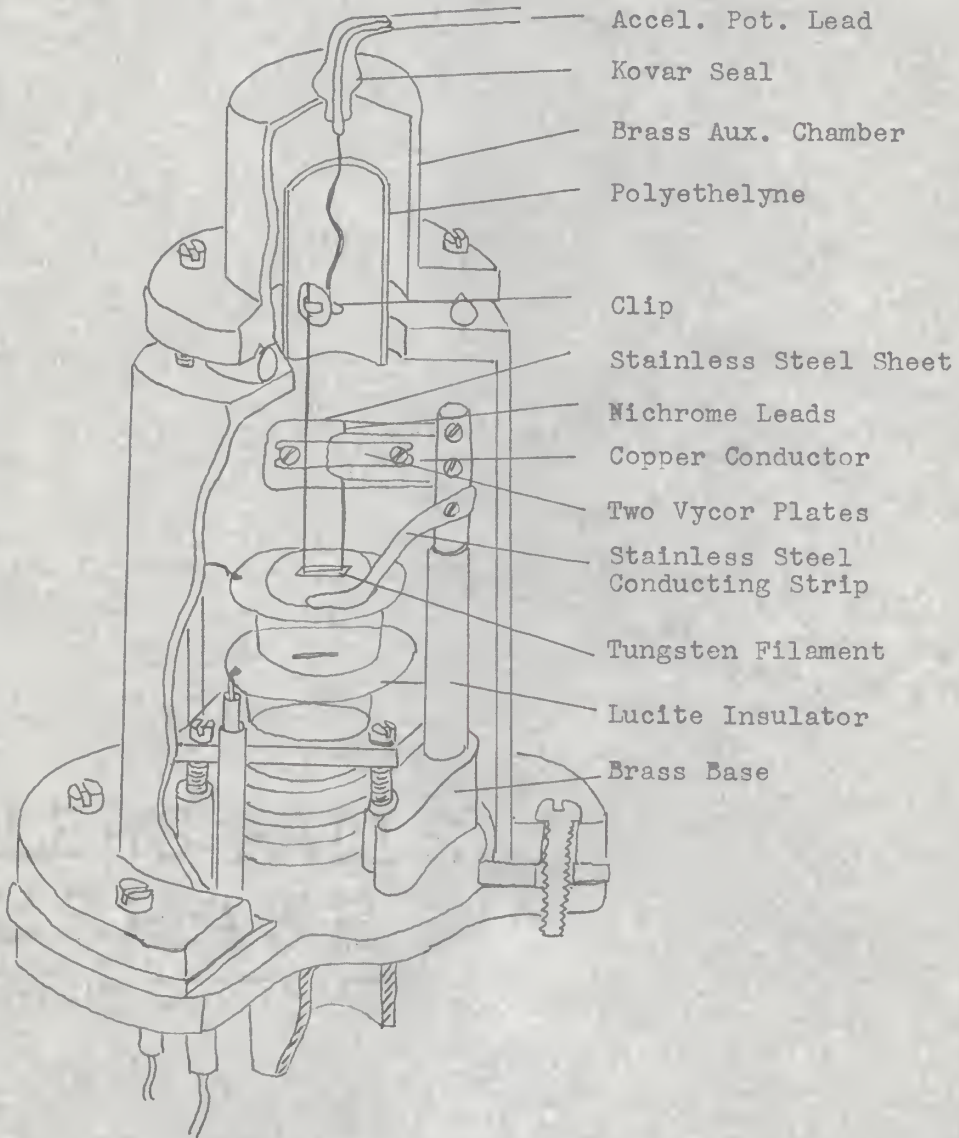
More rigid holders were constructed but the difficulty in positioning the source into the small brass source chamber could not be avoided. The source chamber was removed and a very simple holder with thicker Nichrome leads was constructed. The holder is shown in Plate II.

An auxiliary chamber was constructed to contain the accelerating potential lead, to make connection to the filament simpler and easier, and to take up the slack, heavy lead when the source chamber was closed.

EXPLANATION OF PLATE II

Sketch of source chamber, auxiliary chamber, and filament holder.

## PLATE II





The only disadvantage to this source was the 20-minute operation of opening and resealing the three vacuum seals connecting the auxiliary chamber to the source chamber and the source chamber to the instrument and to a diffusion pump. The advantages were rigidity of source, less distortion of the filament, and a simpler removal of the filament leads for insertion of another sample.

There is no regulation of the filament current. Large deviations in the current, and consequently in the filament temperature, were always observed. Fluctuations in beam current decreased, however, as the source became aged.

Beam currents of three to four microamperes were easily obtainable. The filament was coated by the method described by Hartke.

### The Magnetic Field

Both magnet coils accidentally became grounded to the instrument. The entire instrument was tilted and braced for easy removal of the coils. Rewinding was found unnecessary; the inner surface of each coil through which the core fit had only to be insulated with electrical tape.

Tilting the pole pieces did not disturb the vacuum-tight seams of the analyzing chamber. The resistance of the coils remained approximately 400 ohms each, the values obtained when the coils were first constructed.

Unfortunately, no field-measuring device for fields above 5,000 gauss was obtainable. The field was estimated to be about 10,000 gauss (More, 10).

### The Detector

Because of frequent vacuum leaks, the multi-exposure camera designed by Hartke was replaced by a single plate and frame, similar to that used by More. A fiducial mark was automatically imprinted on the film when the frame was tightened against the plate holder.

Both Eastman Kodak III-O ultra-violet sensitized plates and Eastman Spectroscopic Safety Film, Type SWR (Experimental), were used. Numerous fine dark lines appeared in several test strips of the SWR (Short Wave Radiation) film upon exposure to daylight and after development in D-19. These lines also were observed in the densely fogged portions of the film upon exposure to a mass spectrum.

### The Vacuum System

The pump-down time for the instrument became unusually long after the first 50 runs. It was found that the multi-exposure camera assembly had developed numerous small leaks about the soft soldered flange. There also was considerable leakage through a flange seam of one of the diffusion pumps, strained by the connections to the cooling system.

Values of  $5 \times 10^{-5}$  mm Hg pressure in three hours were attained, after repairs, as measured with the ionization gauge. In a 24-hour period the pressure was  $1 \times 10^{-5}$  mm Hg as compared to  $1 \times 10^{-6}$  mm Hg as cited by More.

The diffusion pump heaters were operated at normal wattage; the circulation of water, at the rate of 2 liters/minute, was about four times the recommended value.

## RESULTS

The mass spectra of lanthanum, praeeseodymium, and neodymium oxide (in dilute nitric acid) were observed. Plate III illustrates these spectra. The first was taken by Hartke; the mass assignments are his interpretation. The remaining four spectra were taken from about 25 films and plates, of which only about half could be used for comparison. They represent the most "persistent" lines observed by the author. Several additional plates showed no developable images.

In the spectra of praeeseodymium and neodymium, no definite comparison with Hartke's mass assignments could be made. Consequently, in Plate III, these lines may belong to any of the groups of lines found by Hartke.

In the spectra of La-Nd, a line possibly corresponding to  $^{155}\text{LaO}^+$ ,<sup>1</sup> assuming Hartke's interpretation is correct, was observed. Its position, however, was dubious because non-symmetrical curvature was present for the set of plates. Other lines were found to the right of this line but still no definite comparison could be made. The data were not reproducible.

As a possibility, the lines appearing, after development, due to some inconsistency in the film could have been mistaken by

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<sup>1</sup> The notation  $^{139}\text{LaO}^+$  is here used to mean lanthanum oxide, singly ionized, La of mass 139, O of mass 16, mass of ion 155.

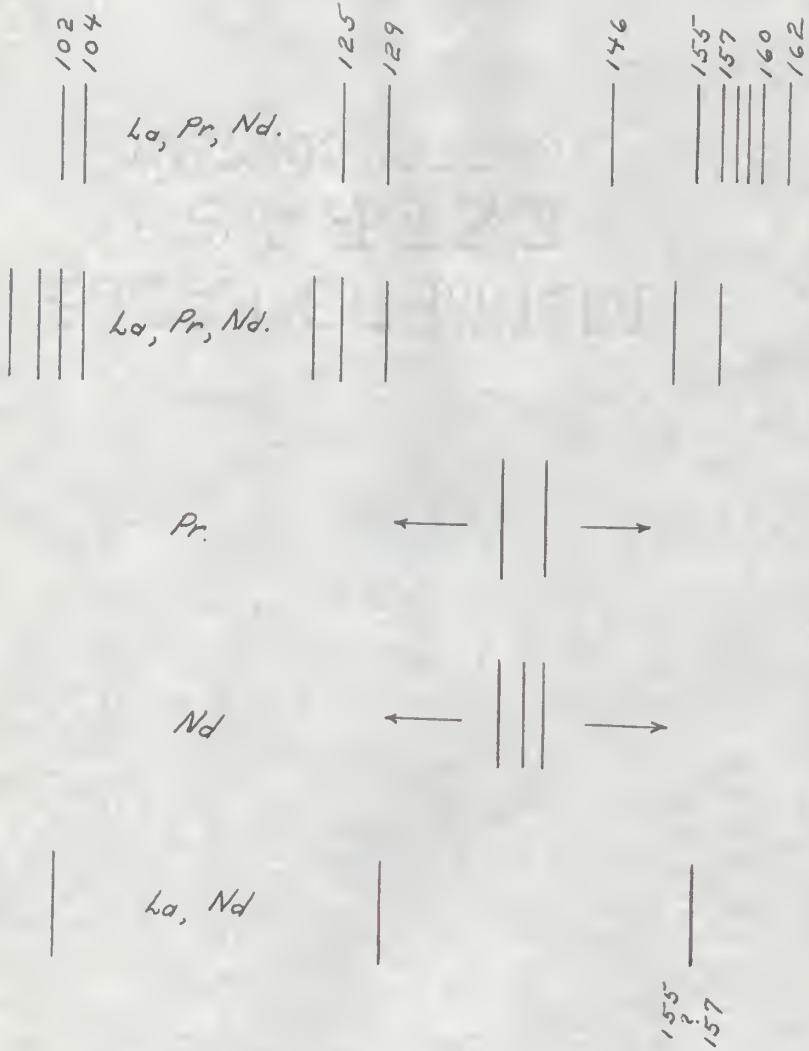
### EXPLANATION OF PLATE III

Mass spectra of praeaseodymium, neodymium, and several combinations of the three rare earths.

The first spectrum and the mass interpretation was taken from Hartke; the remaining spectra are from the author's research.



PLATE III



Hartke as the lines of  $^{142}\text{NdO}^+$ ,  $^{143}\text{NdO}^+$ ,  $^{144}\text{NdO}^+$ , and  $^{146}\text{NdO}^+$ . In close examination of his original film, lines similar to those discussed previously in the section entitled The Detector were observed.

Non-symmetrical curvature of lines was frequently observed, but was found to be due only to distortion of the film. Lines from the Eastman III-O plates were straight; with careful loading of the SWR film, curvature of the lines was no longer observed. The distorted lines did show, however, that the film must be placed closely against the photographic plate holder for a well-focused image.

#### EVALUATION

The mass assignments of the rare earths as suggested by Hartke could not be verified. Nor could any other interpretation be found. Many attempts were made at producing mass separation, only to end in electronic or vacuum difficulties. Nearly 30 per cent of all the runs proved futile.

As a separator of radioisotopes, the instrument, then, lacks stability. To run the instrument with a radioactive sample frequently without a developable line appearing on the plate will surely shorten the life time of the instrument through contamination.

For analysis, there still remains the task of positive identification, providing filament current regulation, and a reduction of line width, a most tedious and predominantly empirical operation.

## ACKNOWLEDGMENTS

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Charged particles of the same energy, but differing in mass, are acted upon by forces of different magnitudes under the influence of a magnetic field. This principle is the basis of mass spectroscopy.

A mass spectrograph previously designed and constructed for the quantity separation of radioisotopes and for analysis of the rare earths was investigated.

Prior to the process of separation, a new and simpler hot anode source holder, in which the filament leads were held in place between two Vycor plates, was constructed. Some of the advantages were rigidity and simplicity in insertion of a new sample.

Deficiencies in the source holder, in the magnet coils, and in the vacuum system were remedied. However, other defects remain in the magnet power supply and filament stabilization.

Twenty-five spectra of the oxides of Nd, Pr, La-Nd, and La-Pr-Nd in dilute nitric acid were investigated. It was not possible to obtain consistent mass spectra of these elements.