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SPACE CHARGE NEUTRALIZATION IN THE IONIZING BEAM OF A MASS SPECTROMETER

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Space Charge Neturalization in the Ionizing Beam of a Mass Spectrometer

A mass spectrometer ion source structure and its mode of operation are described by which the resolved ion current produced from a given gas concentration in the ionizing chamber can be made one to two orders of magnitude larger than is usually obtained in conventional mass spectrometer ion sources. This structure employs an ionizing chamber whose walls are electrically insulated from each other so they can operate at separate potentials which permit positive ions to be trapped in the ionizing electron beam. The resulting partial neutralization of the electronic space charge allows the use of a higher current density ionizing beam and also increases the effective ionizing volume from which a stable ion current can be extracted. Inherently this mode of operation produces more fragmentation species because it increases the probability of several successive electron impacts on each particle.

Introduction

The control of beam dispersion by the trapping of charged particles of sign opposite that of the beam of interest has been carefully studied[1] and utilized in various devices, including mass separators[2]; however, the principle of space-charge neutralization does not appear to have been employed previously for improving the efficiency of the ordinary electron impact-type of ion source used in laboratory mass spectrometers. For several years a 60-degree mass spectrometer has been used at RCA Laboratories under conditions requiring high sensitivity for detecting small partial pressures of volatilized materials. With this spectrometer, it has been found that partial neutralization of the electronic space-charge by the trapping of positive ions in the ionizing beam can be employed to increase the resolved ion beam intensity by one to two orders of magnitude over that obtainable without such space-charge neutralization. The chief disadvantage of this mode of operation of the source is the increased fragmentation pattern developed because of the increased probability of successive electron impacts on the trapped ions. This mode of operation is thus not desirable in mass spectrometers used for hydrocarbon analysis, but can be quite useful for studies of inorganic materials.

[1] L.M. Field, K. Spangenberg, and R. Helm, *Elec. Comm.* **24**, No. 1 108 (1945).

[2] L.P. Smith, W.E. Parkins, and A.T. Forrester, *Phys. Rev.* **72**, 989 (1947).

The Ionizing Chamber

Figure 1 shows the type of ionizing chamber employed. This ionizing chamber differs from that in the ion generating assembly described by Nier[3] mainly in having all walls of the chamber insulated electrically from each other so that all wall potentials can be adjusted independently. (In practice, the walls S could usually be connected directly to A_1 without deleterious effect. Connection to A_1' was not so satisfactory). In addition, the blocks, b, on the ion extraction side have been added to diminish the penetration of the field produced by the voltage difference between plates B and C. With this penetration so diminished, the extraction of ions from the electron beam region depends almost entirely on the cross field between plates B and P. The cathode K is a thoriated tantalum filament of the design described by F. H. Nicoll[4].

Low impedance voltage supplies are indispensable for the maintenance of optimum adjustment of the ion source electrode potentials at high current levels. Motorboating and bi-stable non-optimum operating conditions occur if high impedance voltage supplies are used. For this reason, cathode followers were employed to tap electrode voltages from a stabilized power supply.

[3] A.O. Nier, *Rev. Sci. Inst.* **18**, 398 (1947).

[4] F.H. Nicoll, Letter to the Editor, *Review of Sci. Instruments*, Vol. 26, p. 1206, (1955).

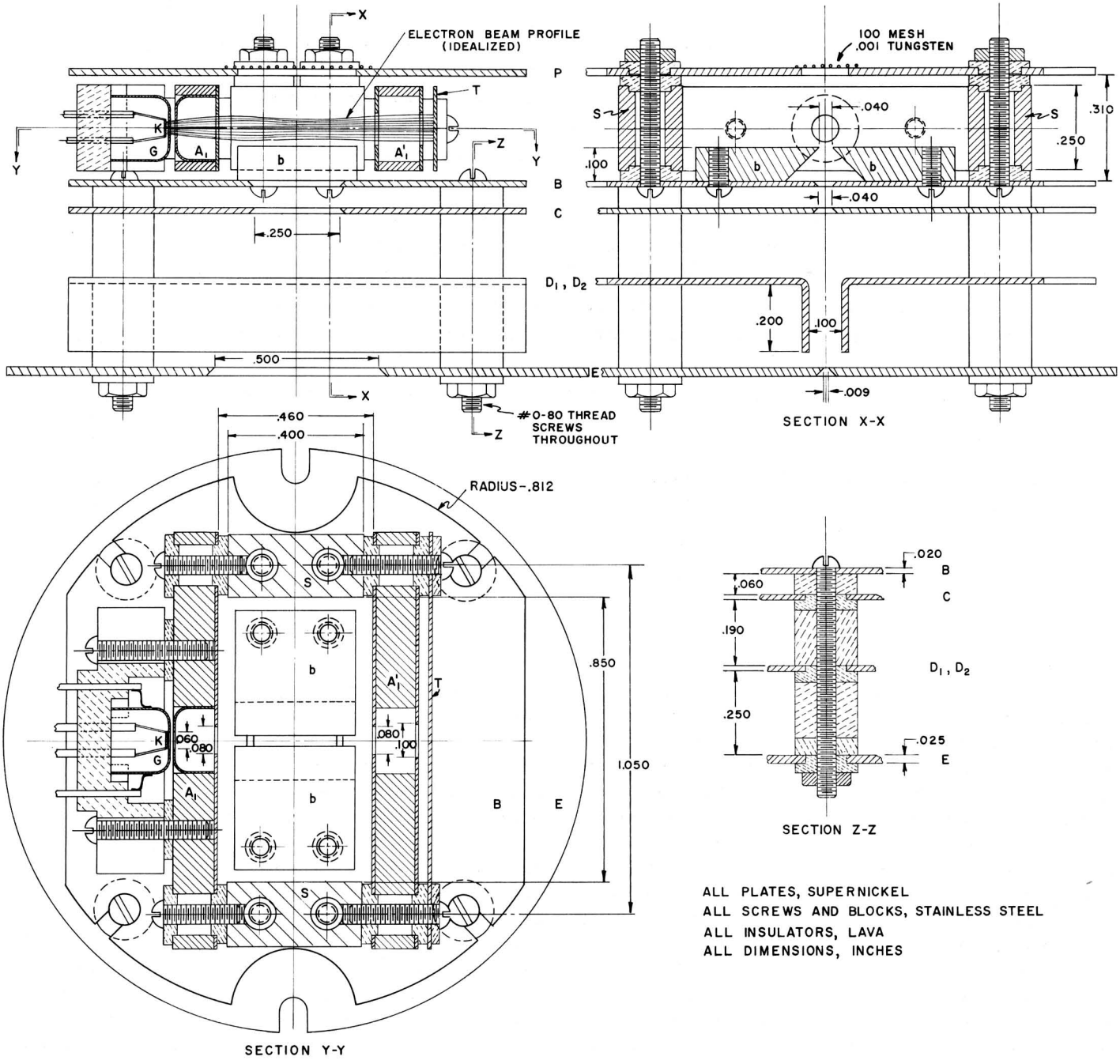

Fig. 1 – Ion source assembly.

Operating Characteristics

Table I gives a typical set of measured electrode potentials and current values for producing the maximum resolved ion current from the principal *Hg* isotope present at a partial pressure of about 1×10^{-8} *mm* in the residual gas (total pressure about 10^{-7} *mm*) of the ionizing chamber. For each trap current value I_T^- (in ma.), corresponding to an ionizing beam-current density J (in ma/cm^2), all electrode potentials were adjusted to maximize the resolved ion current I_{Hg}^+ (in amperes). The value of I_T^- was controlled by changing filament temperature. The electron beam, collimated by the usual axial magnetic field fixed at about 225 gauss, had a maximum useful ionizing volume about 0.2 cm in diameter and 1.2 cm long.

For optimum ion peak height, A_1 must be more positive than A_1'. This prevents ions formed in the potential trough of the electron beam from being drawn along the axis of the electron beam into the cathode. The voltage difference values for A_1-A_1' decrease with electron beam

TABLE I

Electrode Potentials and Currents Measured for Operation of Ionizing Chamber of Fig. 1 Ion Source. Voltage Values are given as Differences between Potentials of Electrodes labelled on Fig. 1. The partial pressure of the Hg^{202} was estimated at about 1×10^{-8} mm. from the source sensitivity calibration. The electron trap T was about 200 volts positive with respect to the cathode K.

Potential Differences (Volts) Between Electrodes of Ion Source						Electron Currents Collected (ma)			Ionizing Beam Current Density $J(ma/cm^2)$	Resolved Ion Beam Current $(Amps \times 10^{13})$ $I^+_{Hg\ 202}$
A_1-K	A_1'-K	B-K	P-K	P-B	G-K	I_{A_1}	$I_{A_1'}$	I_T		
80	72	64	78	14	16	.62	.16	2.0	64	46
80	76	67	72	5	14	.36	.08	1.6	51	30
80	75	70	70	~ 0	14	.22	.07	1.0	32	17
80	75	70	71	1	10	.20	.07	1.0	32	20
80	77	72	76	4	10	.12	.02	0.50	16	7.2
80	79	74	77	3	12	.06	.02	0.30	9.5	5.2
80	79	75	78	3	12	.04	.02	0.23	7.3	4.0
80	80	75	80	5	12	.04	.02	0.23	7.3	1.0

current density as the potential trough becomes more shallow. Similarly, a lower cross-field, P-B voltage, is required to spill ions from the electron beam and push them into the ion accelerating field between plates B and C. In practice, as the electron beam current density diminishes, the optimum P-B voltage goes through a minimum and then rises again to a new maximum value. This latter is determined by the relationship between the exit slit width of the analyzer and the spread in beam energy produced by the potential range of the region of origin of the ions in the P-B field. Incidentally, the adjustment of the A_1-A_1' voltage can also be used to compensate for a mechanical mis-alignment of the lens assembly which might otherwise give the ions a velocity component parallel to the ionizing beam and cause them to wander off the central plane of the analyzer tube before reaching the ion collector.

From an approximate solution of Poisson's equation, one can estimate that the potential in the center of the 80-ev ionizing electron beam having a current density of 50 ma/cm² would be about 5.4 volts lower than that at the beam edge if no neutralization of the space charge is produced by positive ions in the electron beam, hence, space-charge neutralization is clearly important to the efficient extraction of ions and to the production of a relatively mono-energetic ion beam.

For the Table I data, the resolved ion current I^+_{Hg} (in amperes) varies with ionizing beam current density J(in ma/cm²) according to the equation.

$$I^+_{Hg} \simeq 10^{-13}\,(0.50\,J + 3.4 \times 10^{-3}\,J^2)$$

The variation of ion yield with J^2 is somewhat surprising, but is probably due to the convergence of ions into the potential minimum of the partially neutralized electron beam from the outer regions of the beam so that the effective ionizing volume from which ions are extracted and utilized increases with current density. This is possible because the electron beam sweeps a cylindrical path of diameter roughly 10 times the width of the narrowest slit in the ion lens assembly. For low-current operations in which electron beam space charge does not complicate ion extraction, the sensitivity of a well-aligned lens assembly is roughly (within a factor of ten) that computed from the ionization cross section of the neutral species, the partial pressure of the species, and the ionizing current, with the assumption that only those ions are utilized which are formed in the ionizing volume projected upon the narrowest slit of the lens assembly (i.e., that the ion lens system does essentially no concentrating or focusing of ions drawn from the ionizing volume.

Comparison of the data in the last two rows of Table I shows that, even at the lowest ionizing current density used here, the optimum adjustment employing ion trapping (next-to-last row of data) produces a somewhat larger resolved ion current than that adjustment (last row

of data) simulating the usual type of ionizing chamber having five equi-potential walls and a "pusher potential" wall for extracting the ions.

For any particular ionizing chamber structure, it is apparent that plots of ion yield versus ionizing beam current density must eventually decline from the square-law dependence and saturate. This saturation limit decreases with total gas pressure because, for a fixed beam current density, the fraction of all ions formed which must be conserved for appropriate partial neutralization of the electronic space charge increases as the pressure decreases. Thus as the pressure diminishes, the maximum usable stable electron and ion beam currents decrease and also the yield of usable ions per electron diminishes. For our particular ionizing chamber structure, stable operations with electron current densities as high as 125 ma/cm^2 have been obtained without complete saturation in ion yield. For these operations, the total pressure was about 10^{-6} mm; however, at a total pressure around 10^{-8} mm, instabilities and incipient yield saturation were apparent at an electron beam current density around 30 ma/cm^2.

In principle, an ionizing chamber can be constructed in which ions formed in an ionizing path much longer than the final slit of the ion lens assembly are made to drift to the region opposite the extracting slit. To achieve this, the electron beam must be focused so that a maximum in current density in the beam occurs opposite the center of the slit, as shown by the idealized beam profile in Fig. 1. At high current densities, with suitable space-charge neutralization by ion trapping, the effective ionizing volume from which ions are extracted for use can be enlarged in length and diameter considerably above that commonly in use.

Ion trapping obviously increases the probability of successive electron impacts and increases fragmentation of species, hence the ion trapping mode of operation is not desirable for routine analytical spectrometers. Evidence of the occurrence of ion trapping and multiple electron impacts on the trapped ions is shown by the *Hg* spectrum for which, with the electrode adjustments of Row 1 Table I, the relative resolved ion currents were

$$I_{Hg^+} : I_{Hg^{+2}} : I_{Hg^{+3}} : I_{Hg^{+4}} : I_{Hg^{+5}} \simeq 100 : 62 : 42 : 22 : 1$$

(The fifth ionization potential of *Hg* is given as about 82 volts[5], hence little or no Hg^{+5} should be present in the spectrum). By contrast, the relative ionization cross sections for single electron impact ionization[6] of *Hg* with 80 ev electrons to produce the ions Hg^+, Hg^{++}, Hg^{+3} are

$$Q_I : Q_{II} : Q_{III} \simeq 100 : 14 : 0.45.$$

The ion trapping mode of source operation is recommended for special applications such as those demanding high sensitivity or the generation of multiply charged ions and other highly fragmented species.

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[5] G. Herzberg, *Atomic Spectra and Atomic Structure,* p. 201, Prentice-Hall, Inc., N.Y. (1937).

[6] H.S.W. Massey and E.H.S. Burhop, *Electronic and Ionic Impact Phenomena,* p. 38, Oxford Clarendon Press, England (1952).

R. H. Plumlee

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