The Field Within a Commercial EI/FI Source of a Mass Spectrometer

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A novel method for the calculation of the potential distribution in a mass spectrometer source is presented. It consists in solving a Green integral equation and applies both to the FI and EI mode of a CEC 21-110 C mass spectrometer source.

Introduction

Since the advent of field ionisation mass spectrometry (FIMS) [1, 2], field ionisation kinetic (FIK) measurements have become very important for the calculation of rate constants. This was recently reviewed [3]. For the calculation of the experimental rate constant [4] the exact knowledge of the electrostatic field between the razor blade anode and the cathode in the FI source of a commercial EI/FI mass spectrometer is required. Up to now all calculation methods [5] were based on the approximation of the razor blade geometry by a parabolic cylinder, except that based on linear overrelaxation [6].

This paper presents a novel and elegant calculation method of the potential distribution within the FI source, solving a Green integral equation. The method is based on the experimental geometry and is easily fitted into a computer program.

The same method was also used to calculate the potential distribution in the electron ionization (EI) mode, again taking into account real conditions of geometry and of potentials in the ionization chamber.

A) Theory

Electrostatic and electromagnetic field problems can numerically be solved making use of integral equations, especially when the geometry is of great importance, as shown by De Mey in the case of the field problem of a Hall [7a, b] generator.

In many cases linear problems which can be described by partial differential equations with specific boundary conditions may also be described by an equivalent integral equation. The only condition is that a particular solution of the partial differential equation is known, the so called "Green's function".

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The Green's function of the Laplacian for an infinite two dimensional system is given by [8]

$$G(\bar{r}\,|\,\bar{r}_i) = \frac{1}{2\pi\varepsilon_0} \ln \frac{1}{|\bar{r}-\bar{r}_i|}. \qquad (1)$$

Accordingly, the potential in a point $\bar{r}$ within a finite two dimensional system delineated by a contour is given by a linear combination of Green's functions, with all $\bar{r}_i$ belonging to the contour:

$$U(\bar{r}) = \frac{1}{2\pi\varepsilon_0} \oint_C \varrho(\bar{r}_i) \ln \frac{1}{|\bar{r}-\bar{r}_i|}\, \mathrm{d}C_i. \qquad (2)$$

As boundary conditions for this problem should be taken the potentials $U_0(\bar{r})$ in each point of the circumscribed contour: $\bar{r} \in C$. This contour may be of any whimsical shape on condition that it be closed and that the interval between two different points (and potentials) can analytically be described.

Application of the same solution to the points of the contour themselves results in an integral equation with $\varrho(\bar{r})$ as unknown function:

$$U_0(\bar{r}) = \frac{1}{2\pi\varepsilon_0} \oint_C \varrho(\bar{r}_i) \ln \frac{1}{|\bar{r}-\bar{r}_i|}\, \mathrm{d}C_i. \qquad (3)$$

For the numerical solution of the linear integral equation the contour C is divided into n intervals ΔC. For each of these the function $\varrho(\bar{r})$ is approximated by an unknown ϱ_j. For each point $\bar{r}$ belonging to the contour, Eq. (3) transforms to

$$U_0(\bar{r}) = \frac{1}{2\pi\varepsilon_0} \sum_{j=1}^{n} \varrho_j \int_{\Delta C_j} \ln \frac{1}{|\bar{r}-\bar{r}_i|}\, \mathrm{d}C_i \qquad (4)$$

in which $\bar{r}$ is taken at the center of each interval ΔC. A set of linear equations results. This can be written in matrix form: $[U_0] = [A][\varrho]$, from which $[\varrho]$ is calculated using the elimination method of Gauss [9].

The calculational method outlined above will now be applied to the description of the combined EI/FI source of a CEC 21-110 C mass spectrometer.

B) Calculation of the Potential Distribution in Fi Mode between Razor Blade Anode and Cathode

To start with, in Fig. 1 a closed contour is presented, delineated by 10 points (0 to 9). To each of the points 1 to 9 is linked a potential $U_0(\vec{r})$ that was measured accurately and given to the computer together with the coordinates X_i and Y_i and the number n of intervals ΔC between two subsequent points (see Table 1). The potentials in the center of each segment ΔC of the contour from pt. 4 to pt. 5 were found by linear interpolation between the anode- and the cathodepotential. The potential in point 0, the origin of the coordinate system, is one of the potentials to be calculated.

Table 1. Data for the calculation of the y potential gradient in FI mode.

Pt.	n	X_i (unit=0.05 mm)	Y_i	$U_0(\vec{r})$ (V)
1	30	0.0	13.6	8000
2	15	0.2	15.0	8000
3	5	1.0	20.6	8000
4	25	1.0	25.6	8000
5	35	18.0	8.6	−1500
6	35	5.0	8.6	−1500
7	30	3.3	8.6	−1500
8	15	3.3	7.1	−1500
9	10	3.3	0.0	−1500

Once matrix $[\varrho]$ is known from these data, the potential in each point of the two dimensional system can be calculated using Equation (2). The symmetry plane through the y axis is taken into account.

In order to achieve a sufficient spatial resolution two more contours are generated as presented in Figs. 2 and 3, concentrating closer to the razor blade tip. From a former contour the program calculates

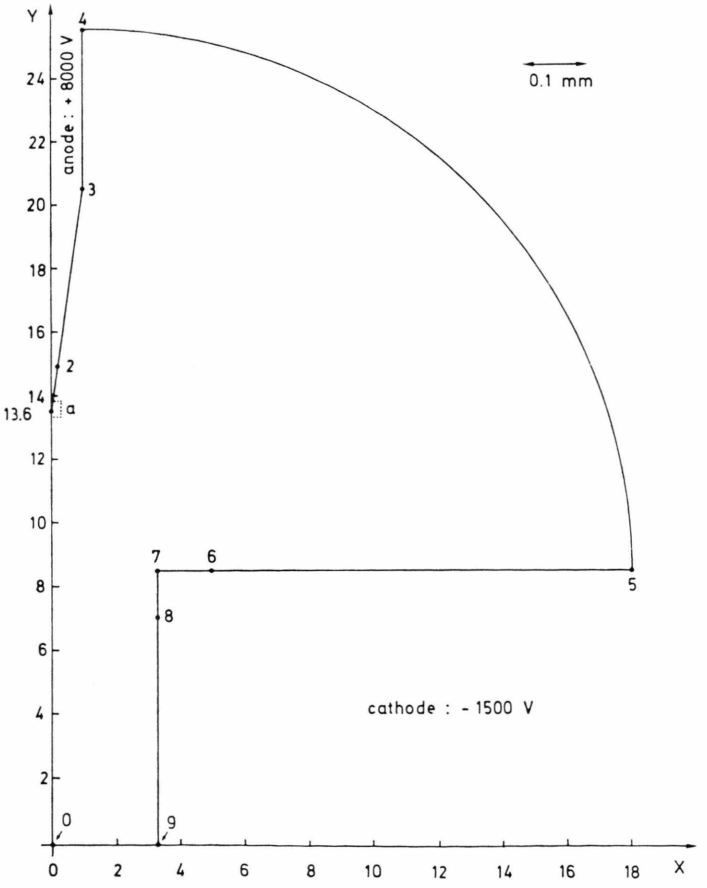

Fig. 1. Closed contour for the roughest potential calculation along the y axis in FI mode. X and Y in arbitrary units, used throughout in Figs. 2 and 3. — The outline a includes pt. 1 and refers to Figure 2.

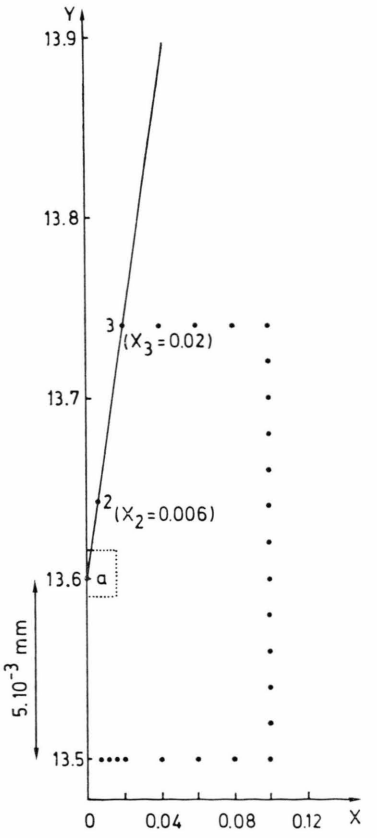

Fig. 2. Closed contour for the first refined potential calculation. — The outline a includes pt. 1 and refers to Figure 3.

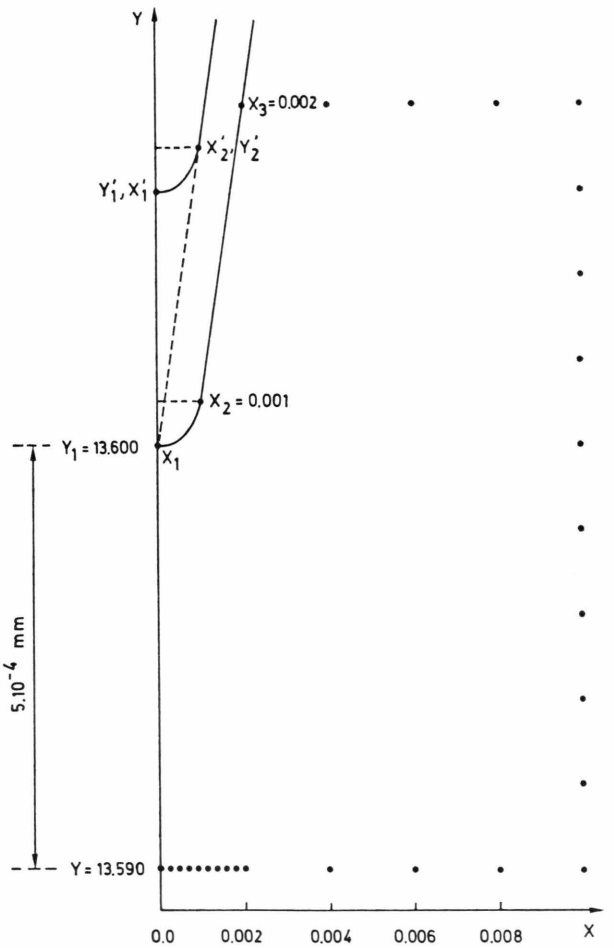

Fig. 3. Closed contour for the narrowest potential calculation. — Taking into account the real curvature at the tip of the edge the coordinates X_i', Y_i' are to be translated to X_i, Y_i.

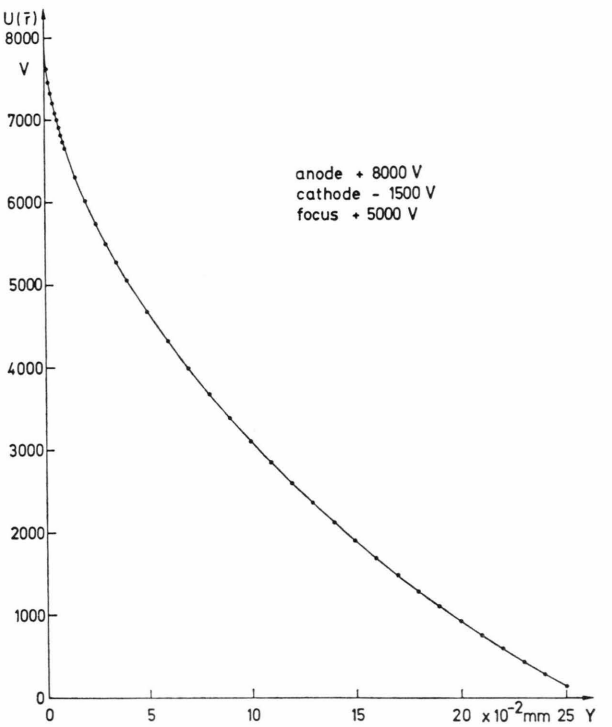

Fig. 4. Potential distribution resulting from the roughest calculation. — Resolution: $0.1 \cdot 10^{-2}$ mm.

the potentials in the defining points of the next contour. The final spatial resolution attains 50 Å.

Results

We have used a Siemens 4004 computer with cycle time $165 \cdot 10^{-9}$ sec/4 bytes. Due to the severe needs of spatial resolution a large matrix [A] is required. However, the larger the matrix [A] the longer the runtime of the computer program. With a 40×40 matrix, less than 50 K memory and only 4.4 sec of runtime are needed, but with a 200×200 matrix, less than 180 K memory and about 250 sec of runtime are needed. The results are presented in Fig. 4 for the following instrument settings: anode $+8000$ V, cathode -1500 V, focus $+5000$ V.

Only the calculation of the potential distribution along the y axis ($X = 0$) is presented although it is trivial that the potential distribution in each direction of the two dimensional system could be found. It is seen that at $25 \cdot 10^{-2}$ mm, the distance from the edge to the cathode slit, the potential is not zero and thus penetrates beyond the cathode slit.

The detailed listing of the calculational results as they are obtained step by step is given in Table 2.

The curve in Fig. 5 represents about fifty calculated points. The inset of the figure shows the first ten points ($0 - 500$ Å). The potential gradient doesn't diverge to infinity as the distance to the edge

Table 2. The groups of calculated points along the y axis.

Number of points	Spatial resolution (Å)	Distance to the edge (in y coord)
10	50	$Y = 0.001$
20	100	$Y = 0.005$
10	250	$Y = 0.01$
45	$1 \cdot 10^3$	$Y = 0.1$
95	$1 \cdot 10^4$	$Y = 2.0$
30	$5 \cdot 10^5$	$Y = 5.0$

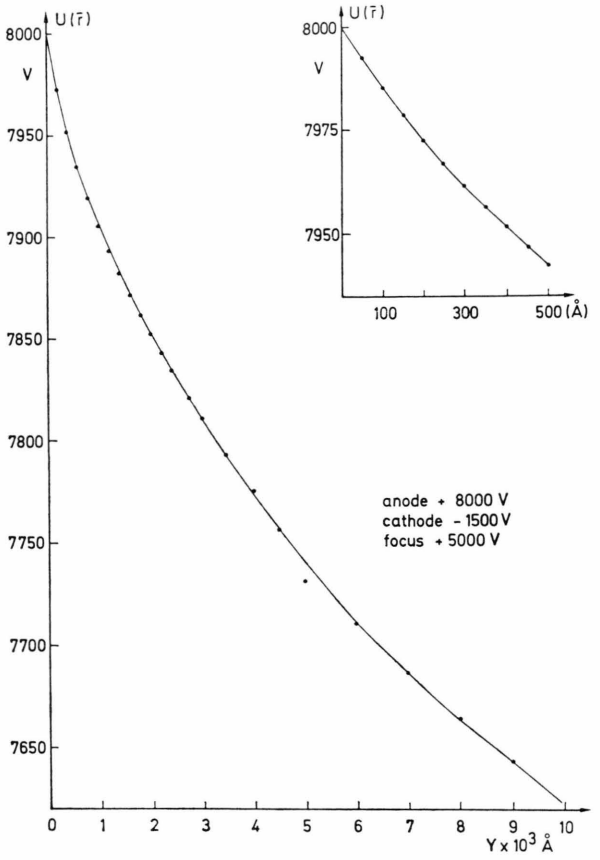

Fig. 5. Potential distribution resulting from the narrower calculation. — Resolution: 250 Å. The inset shows the first 10 calculated points. — Resolution: 50 Å.

approaches 0 because of the real geometry of the razor blade, which was taken as a basis, as suggested in the Fig. 3, with a radius of curvature of 500 Å, after Robertson and Viney [5].

C) Calculation of the Potential Distribution in FI Mode beyond the Cathode

All other calculating methods for the estimation of the potential distribution between anode and cathode cannot be applied for calculating the distribution beyond the cathode. Generally the potential decay is supposed to be that of a plane condensor.

Only the method of linear overrelaxation allows determination of the potential in any point beyond the cathode. The present method of solving a Green integral equation also allows an accurate determination.

The computer again is given the accurately measured potentials in the points 1 to 21 and the coordinates of 22 points (0 to 21) which are shown in Figure 6.

Simultaneously the numbers n of partitions ΔC between two subsequent points are introduced (see Table 3). The contour between points 1 and 2 is divided into 7 partitions ΔC. Resulting from the preceeding part the potential is known to penetrate through the cathode slit. Therefore, the potential in the center of each ΔC (between pt. 1 and pt. 2) is to be previously calculated from the former part.

Results

As there are no special needs of spatial resolution in this part of the potential calculation, a 137×137 matrix has been used resulting in a CPU-time of about 100 sec. The calculated potential distribution throughout the source in the y direction is presented in Figure 7.

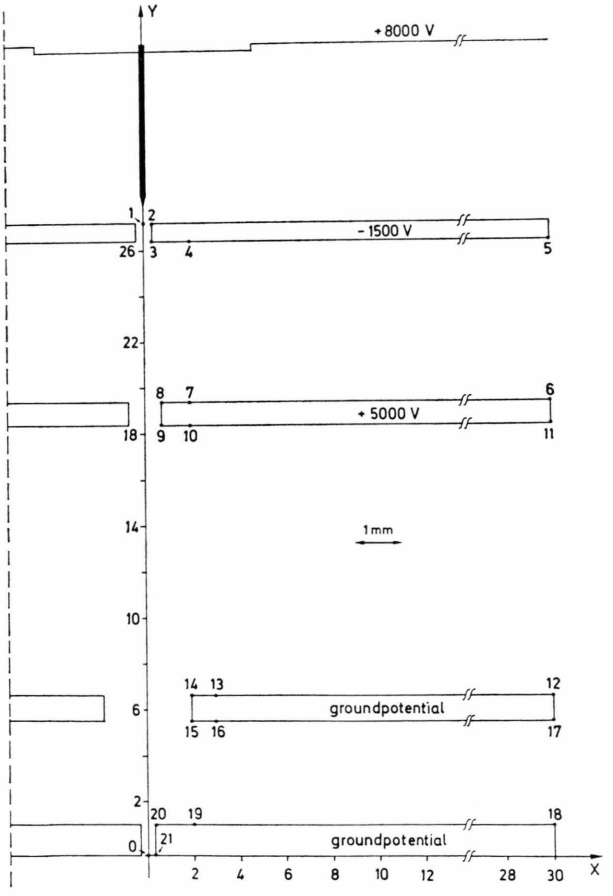

Fig. 6. The contour shape for the potential calculation along the y axis in FI mode beyond the slit cathode; it is closed by connecting the points 1 to 0 through 2, 3, ...

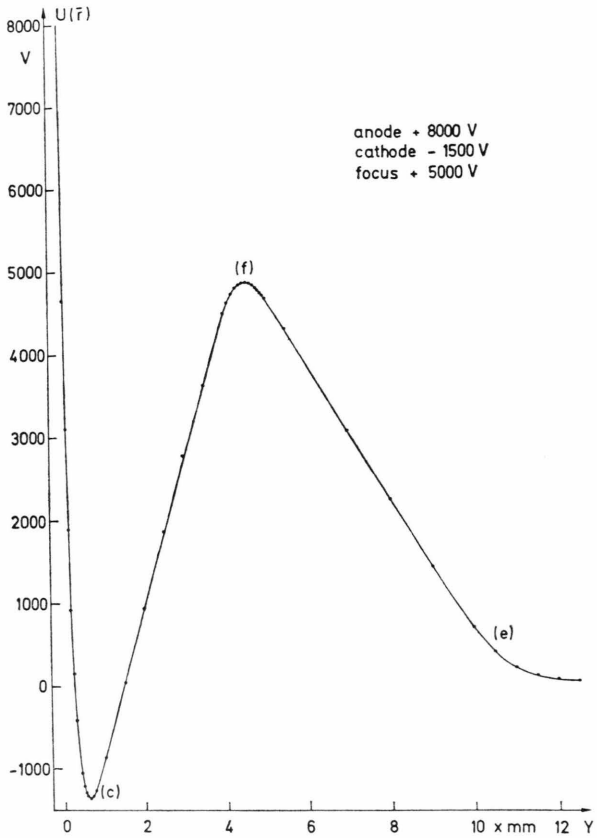

Fig. 7. Calculated potential distribution along the y axis in FI mode beyond the slit cathode; the position of the cathode slit, the focus plates, and the exit slit are at c, f and e, respectively.

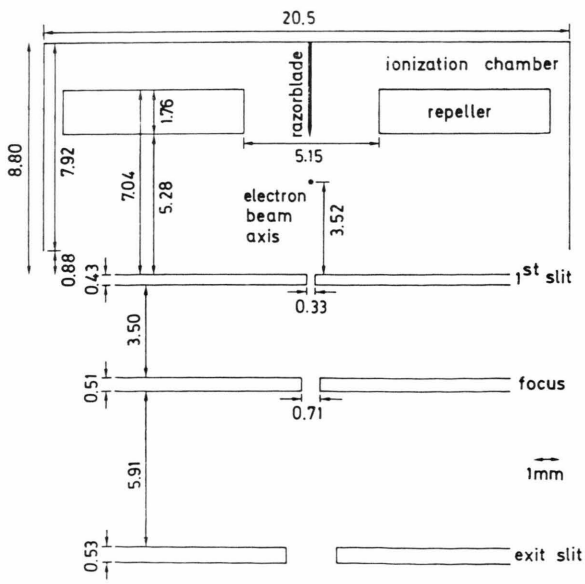

Fig. 8. The dimensions of the EI/FI source of the CEC 21-110 C mass spectrometer. — All dimensions are expressed in mm.

Table 3. Data for the calculation of the potential distribution beyond the cathode in FI mode.

Pt.	n	X_i (unit = 0.5 mm)	Y_i (unit = 0.5 mm)	$U_0(\bar{r})$ (V)
1	7	0.0	27.84	to be calculated
2	7	0.33	27.84	−1500
3	8	0.33	26.98	−1500
4	10	2.00	26.98	−1500
5	3	30.00	26.98	−1500
6	10	30.00	19.98	+5000
7	6	2.00	19.98	+5000
8	9	0.71	19.98	+5000
9	6	0.71	18.96	+5000
10	10	2.00	18.96	+5000
11	5	30.00	18.96	+5000
12	10	30.00	7.14	0
13	4	3.00	7.14	0
14	7	1.90	7.14	0
15	4	1.90	6.08	0
16	10	3.00	6.08	0
17	2	30.00	6.08	0
18	10	30.00	1.50	0
19	4	2.00	1.50	0
20	3	0.30	1.50	0
21	2	0.30	0.00	0

Table 4. Data for the calculation of the potential distribution in EI mode. * Cfr. Table 5, first row.

Pt.	n	X_i (mm)	Y_i (mm)	$U_0(\bar{r})$ * (V)
1	2	0.00	16.16	8000
2	3	0.05	17.00	8000
3	3	0.05	17.92	8000
4	7	0.05	19.68	8000
5	2	6.00	19.68	8000
6	4	6.00	17.92	8087
7	4	2.57	17.92	8087
8	4	2.57	16.16	8087
9	5	4.00	16.16	8087
10	2	9.00	16.16	8087
11	2	9.00	17.40	8087
12	5	10.25	17.40	8000
13	2	10.25	11.76	8000
14	9	10.25	10.88	8000
15	3	1.00	10.88	8000
16	3	0.16	10.88	8000
17	3	0.16	10.45	8000
18	12	1.00	10.45	8000
19	3	13.00	10.45	8000
20	12	13.00	6.95	7242
21	3	1.00	6.95	7242
22	3	0.35	6.95	7242
23	3	0.35	6.44	7242
24	12	1.00	6.44	7242
25	6	13.00	6.44	7242
26	11	13.00	0.53	0
27	2	1.45	0.53	0
28	4	1.45	0.00	0

It may be concluded that a linear decay can be a sufficient approximation for the region beyond the cathode (c) to the focus (f) and for the region between focus and exit slits (e).

D) Calculation of the Potential Distribution in the EI Mode

Calculation of flight times of metastable ions produced by EI as a function of the applied draw-out voltage was a method for determination of rate constants proposed by Momigny [10]. A more general method was presented by Hills et al [11]. Following this paper a CEC 21-110 mass spectrometer can be divided into several parts. The flight times in each part can easily be estimated if the potential distribution in the EI source is accurately known. Calculation of rate constants from experimental ion abundances will be described in a next paper.

For calculation of the potential distribution in the EI source the preceeding method of solving a Green integral equation may again be applied. Now we need the exact knowledge of the dimensions of each part within the ionization chamber of the EI source. These are presented in the Fig. 8 and are partly taken from the literature [12].

Table 5. Experimental voltages used in the potential calculations shown in Figure 10.

Bloc (V)	Repeller (V)	Focus (V)
8000	8087	7242
7000	7075	6375
6000	6062	5464
5000	5053	4553
4000	4043	3644
3000	3032	2728
2000	2022	1817

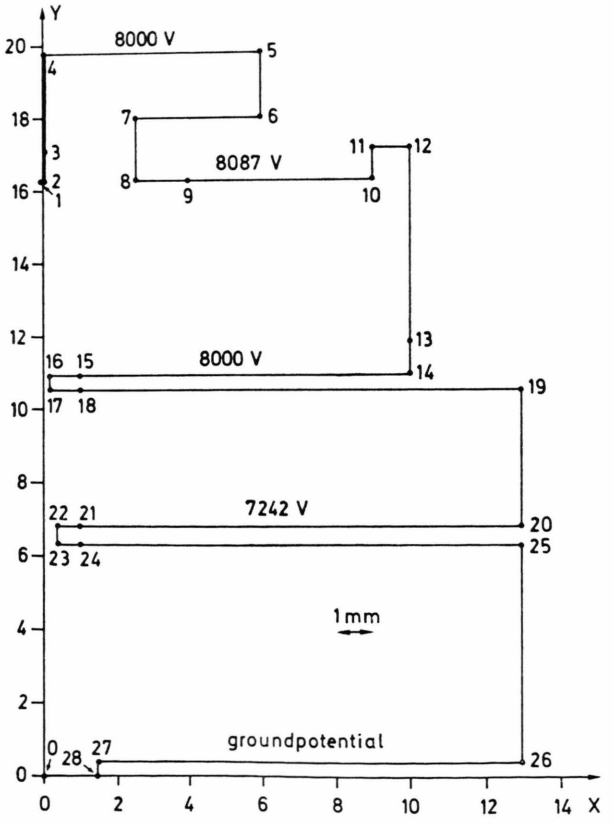

Fig. 9. Closed contour for the potential calculation along the y axis in EI mode taking into account the real geometry of the CEC source shown in Figure 8. — X and Y in arbitrary units.

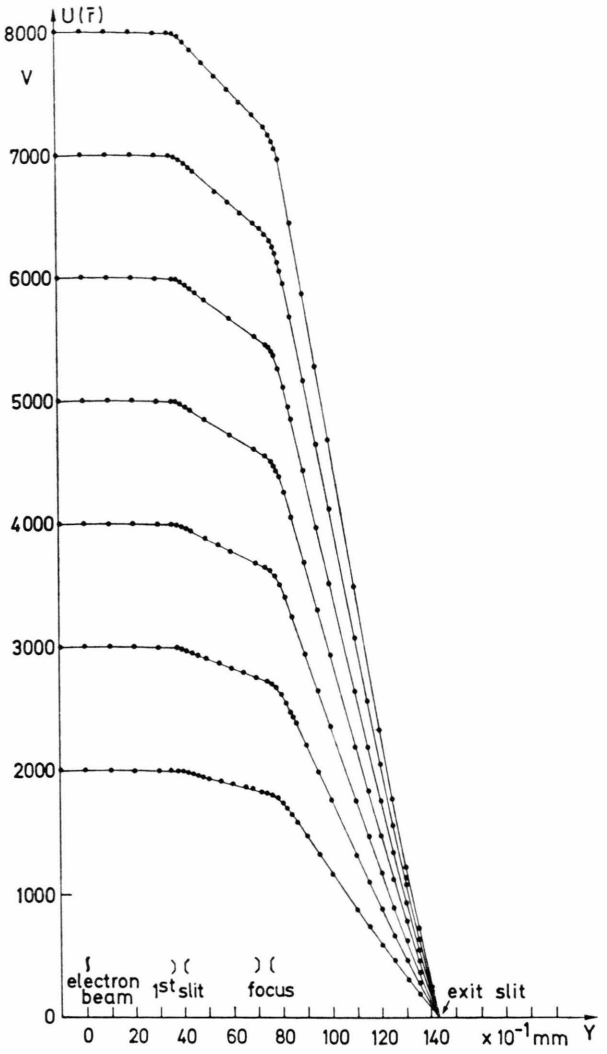

Fig. 10. Potential distribution along the y axis in EI mode for the experimental potential values from Table 5.

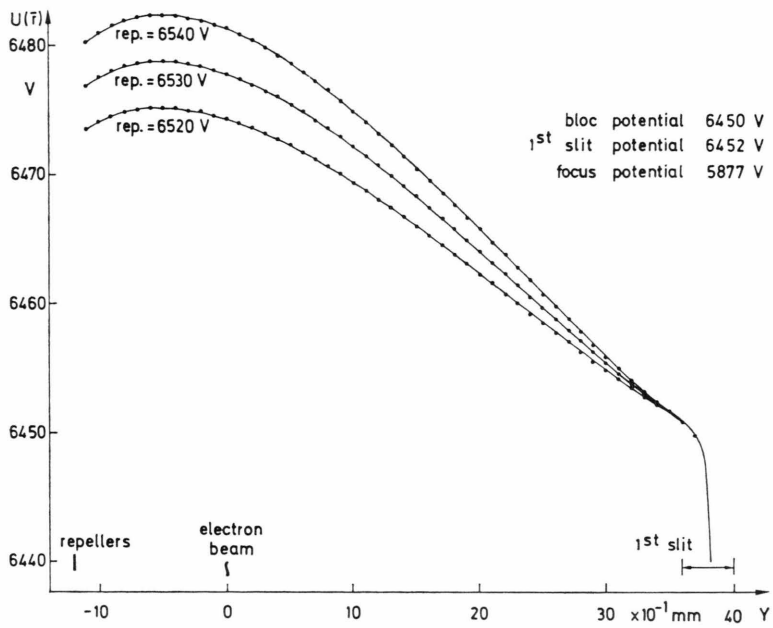

Fig. 11. Potential distribution along the y axis in EI mode, up to the first slit, for different repeller settings.

The Fig. 9 shows half the contour from which the coordinates of 29 points (0 to 28) are defined and given to the computer, together with the numbers n of partitions between two subsequent points which define each interval ΔC (see Table 4).

It is well known that the setting of the potentials of each element of the source is critical to the experimental ion abundances. Therefore it is important that these potentials should be registered after each measurement. Potentials between pts 13 – 14, 19 – 20 and 25 – 26 are supposed to behave as between the parallel plates of a plane condensor.

Results

There is no severe need for spatial resolution. The computer calculates 155 points each at 0.1 mm intervals along the y axis. We therefore make use of a 134×134 matrix and 85 sec CPU-time.

Only the potential along the y axis ($X = 0$) is presented in the Fig. 10 for measured experimental potential values of bloc, repeller and focus (Table 5).

From Fig. 10 it follows that the potential distribution between the beam and the first slit, respectively the first slit and the focus and also the focus and the exit slit can be considered as being nearly linear. However, from Fig. 11, which shows detailed results for a series of experimental high voltage values, in the region between the beam and the focus, it follows that the slope of the linear part of the potential distribution curve depends on the repeller voltage. This is a very important result with regard to ion velocity calculations.

[1] R. Gomer, Field Emission & Field Ionization, Harvard University Press, Cambridge, Mass. 1961.

[2] H. D. Beckey, Field Ionization Mass Spectrometry, Pergamon Press, Oxford 1971 + references.

[3] a) Int. Rev. Sci., Ser. II, Vol. 5 "Mass Spectrometry", A. Maccoll, Butterworths, London 1975 — Ch. I by P. J. Derrick (p. 1). — b) A. L. Burlingame, B. J. Kimble, and P. J. Derrick, Anal. Chem. **48 (5)**, 369R [1976].

[4] H. D. Beckey, K. Levsen, and P. J. Derrick, O.M.S. **11**, 835 [1976].

[5] a) A. J. B. Robertson and B. W. Viney, Adv. Mass Spectr. **3**, 23 [1966]. — b) D. F. Brailsford and A. J. B. Robertson Int. J. Mass Spectr. & Ion Phys. **1**, 75 [1968]. — c) J. M. Gilliland and B. W. Viney, Royal Aircraft Estn. Tech. Rep. nº 68271, 1968. — d) D. F. Brailsford, J. Phys. D: Appl. Phys. **3**, 196 [1970].

[6] J. P. Pfeiffer, A. M. Falick, and A. L. Burlingame, Int. J. Mass Spectr. & Ion Phys. **11**, 345 [1973].

[7] a) G. De Mey, Electronics, Letters **9** (12), 264 [1973]. — b) S. De Wolf and G. De Mey, Information Proceeding Letters **3**, 121 [1975].

[8] a) G. Arfken, Mathematical Methods for Physicist, 2e Ed., Acad. Press New York 1970. — b) G. De Mey, Doctoral Thesis 1975.

[9] a) A. Ralston and H. S. Wilf, Mathematical Methods for Digital Computers, John Wiley, New York 1967. — b) IBM-subroutine GELG, SSP-III [1970].

[10] J. Momigny, Bull. Soc. Chim. Belges **70**, 291 [1961].

[11] L. P. Hills, J. H. Futrell, and A. L. Wahrhaftig, J. Chem. Phys. **51**, 5255 [1969].

[12] Ref. [6], p. 346.