Pühajärve, May 31, 2004

Review of methods of air ion measurement

Hannes.Tammet@ut.ee

ION(ienai): *Michael* ***Faraday*** *(& William Whewell)*

Faraday, M. (1834) Experimental researches on electricity, 7th series.
Phil. Trans. R. Soc. (Lond.) **124**, 77–122.

Dissociation: ***Svante August Arrhenius***

Dissertatio Academiae Upsalensis:
(passed with fourth grade) (Ostwald in Uppsala August 1884)

Arrhenius, S.A. (1884) *Recherches sur la conductibilité galvanique des électrolytes*. 1–2. Stockholm. ii + 64; + 90 pp. + 1 plate.

Arrhenius, S. (1887) Ueber das Leitungsvermögen der phosphorescirenden Luft. *Ann. Phys.* **32**, 545–572.

Leitungsvermögen phosphorescirender Luft. 545

II. ***Ueber das Leitungsvermögen der phosphorescirenden Luft; von Svante Arrhenius.***

(Der schwedischen Academie der Wiss. mitgetheilt den 14. Sept. 1887.)

(Hierzu Taf. IV Fig. 1—3.)

1. Einleitung; Versuchsmethode.

Die Versuche, worüber unten berichtet wird, sind im physikalischen Institut der Universität Würzburg während des Wintersemesters 1886—1887 ausgeführt. Für die freundliche Unterstützung, welche mir dabei von Seiten des Vorstandes dieses Instituts, Hrn. Prof. Friedrich Kohlrausch, zu Theil geworden ist, erlaube ich mir hier meinen verbindlichsten Dank auszusprechen.

NB: No reference to *Giese* (1882)!

Giese, W: (1882) Experimentelle Beiträge zur Kenntniss vom elektrischen Leitungsvermögen der Flammengase. *Ann. Phys.* **17**, 1–41 + 236–257 + 519–550. (95 pp.)

1882. ANNALEN № 9.
DER PHYSIK UND CHEMIE.
NEUE FOLGE. BAND XVII.

I. *Experimentelle Beiträge zur Kenntniss vom electrischen Leitungsvermögen der Flammengase;*

von W. Giese.

1) Während das electrische Leitungsvermögen der Flammen in neuerer Zeit Gegenstand zahlreicher und eingehender Arbeiten gewesen ist, hat sich die Aufmerksamkeit der Experimentatoren nur in geringem Maase den Leitungsvorgängen in der über einer Flamme aufsteigenden Gassäule zugewendet, die den Gegenstand dieser Untersuchung bilden werden.

$$[k g_N \, dw]_2 - [k g_N \, dw]_1$$
$$= \int d\tau \left\{ \frac{\partial}{\partial x}\left(K \frac{\partial V}{\partial x}\right) + \frac{\partial}{\partial y}\left(K \frac{\partial V}{\partial y}\right) + \frac{\partial}{\partial z}\left(K \frac{\partial V}{\partial z}\right) \right\}.$$

Rechts ist das Oberflächenintegral gleich in ein Raumintegral verwandelt. Bezeichnet μ die Dichtigkeit der Gase, so muss des stationären Zustandes wegen $\mu g_N dw$ für alle durch den Faden gelegten Schnitte dw den gleichen Werth m haben, sodass die linke Seite:

$$\left[\left(\frac{k}{\mu}\right)_2 - \left(\frac{k}{\mu}\right)_1\right] m$$

wird. Beschränkt man den Integrationsraum auf ein Fadenelement, so kommt:

$$(\mathrm{I_b}) \qquad m \, . \, \frac{d}{d\tau}\left(\frac{k}{\mu}\right) = K \Delta V + \frac{\partial K}{\partial x} \cdot \frac{\partial V}{\partial x} + \frac{\partial K}{\partial y} \cdot \frac{\partial V}{\partial y} + \frac{\partial K}{\partial z} \cdot \frac{\partial V}{\partial z}.$$

Falls K constant ist, lässt sich die Integration unmittelbar vollziehen, sie gibt:

$$(4) \qquad \frac{k}{\mu} = \frac{k_0}{\mu_0} \cdot e^{-\int_0^\tau d\tau \, \frac{4 \pi K \mu}{m}}.$$

den Draht versetzt werden sollte. Es wird also eine rein mechanische Ursache für das Leitungsvermögen zu suchen sein. Nun sind diejenigen Leiter, für welche man sich bis jetzt die bestimmtesten Vorstellungen über den Mechanismus der Leitung gebildet hat, die Electrolyten; man nimmt für sie an[1]), dass es einzelne, schon vor Eintritt des electrischen Vorganges im Electrolyten vorhandene Atome oder Atomgruppen, welche für sich keine geschlossenen Molecüle bilden, die sogenannten Ionen seien, welche den Vorgang der Stromleitung vermitteln, indem sie sich in Richtung der Kraftlinien fortbewegen und dabei electrische Ladungen mit sich führen. Im ersten Anschluss an diese Vorstellung soll angenommen werden, dass auch in den Gasen das Leitungsvermögen an das Vorhandensein von Jonen in dem soeben definirten[2]) Sinne gebunden sei. Nach den herrschenden Anschauungen über die Constitution der Gase sollten sich Ionen in jedem Gase schon bei gewöhnlicher Temperatur und Atmosphärendruck vorfinden, wenn auch in geringer Menge; mit steigender Temperatur wächst ihre Zahl. Speciell für atmosphärische Luft würden wir nach den Ergebnissen der §§ 54 und 55 anzunehmen haben, dass bei Temperaturen unter 100° zu wenig Ionen, d. h. einzelne Stickstoff- und Sauerstoffatome vorhanden seien, um eine für unsere Apparate wahrnehmbare Electricitätsleitung zu vermitteln, dass aber bei Berührung mit dem glühenden Draht eine hinreichende Anzahl Ionen durch Zertrümmern von Molecülen gebildet wird, um merkliche Electricitätsmengen leiten zu

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1) Clausius, Pogg. Ann. **101.** p. 345. 1857.

2) Die Definition weicht insofern von der üblichen ab, als man unter Ionen gewöhnlich Bestandtheile eines Salzmolecüls versteht.

Summary of the 19th century knowledge:
Thomson, J.J. (1898) *Discharge of electricity through gases*. Westminster.

STUDENTS OF THOMSON

John Zeleny

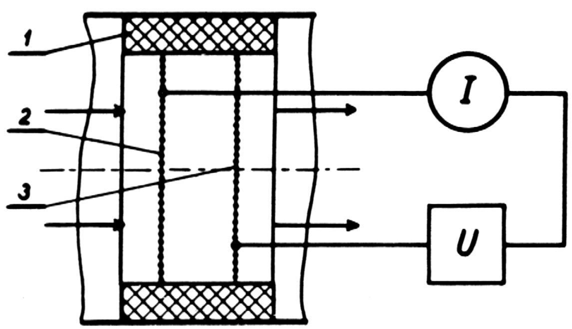


FIGURE 6.3. Counter in which air is blown through grids:

1—insulator; 2—collector grid; 3—repulsing grid.

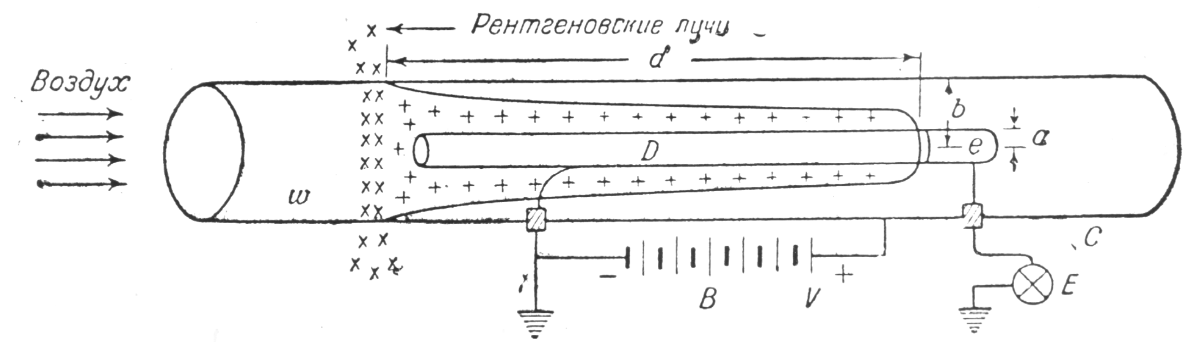


Рис. 1. Первоначальный метод Зелени. Пучок рентгеновских лучей показан косыми крестиками.

Ernest Rutherford:

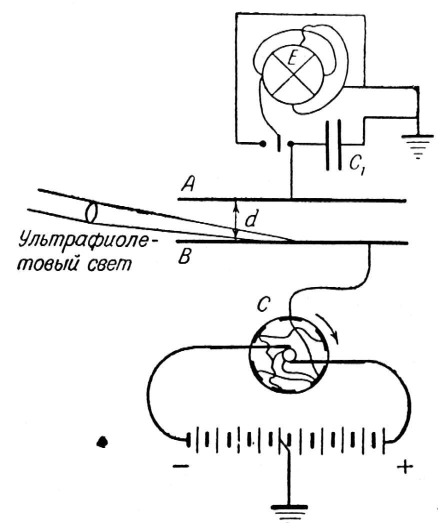


Рис. 6. Метод Резерфорда переменного тока.

ATMOSPHERIC IONS

Actually, the conductivity of the natural air was proved at first by Richmann in St. Petersburg and exactly measured by Coulomb (1785) in Paris.
The mechanism of conductivity was not known this time.

Elster, J., Geitel, H. (1899) Über die Existenz elektrischer Ionen in der Atmosphäre. *Terr. Magn. Atmos. Electr.* **4**, 315–329.

Ebert, H. (1901) Aspirationsapparat zur Bestimmung ded Ionengehalts der Atmosphäre. *Phys. Z.* **2**, 662–664.

Gerdien, H. (1905) Demonstration eines Apparates zur absoluten Messung der elektrischen Leitfähigkeit der Luft. *Phys. Z.* **6**, 800–801.

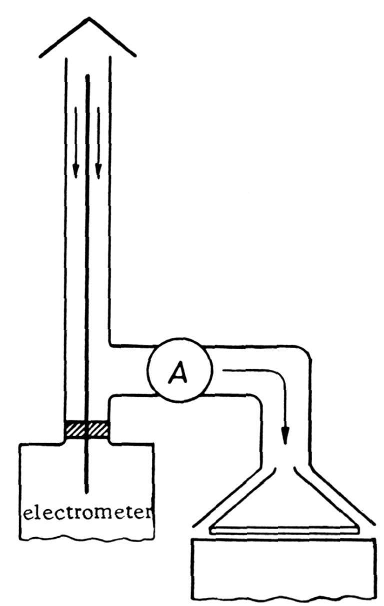


FIGURE 103. Schematic diagram of the Ebert ion counter.

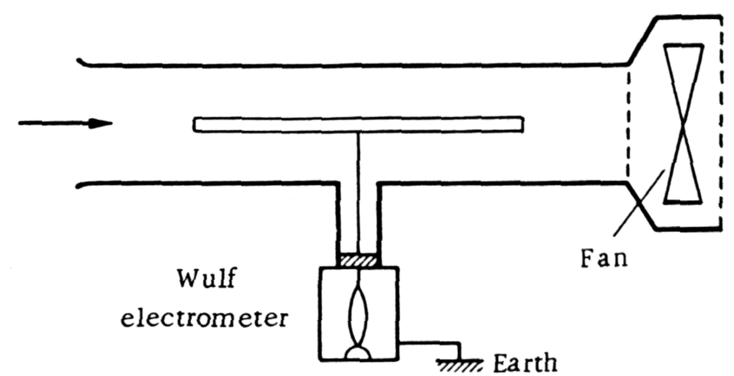


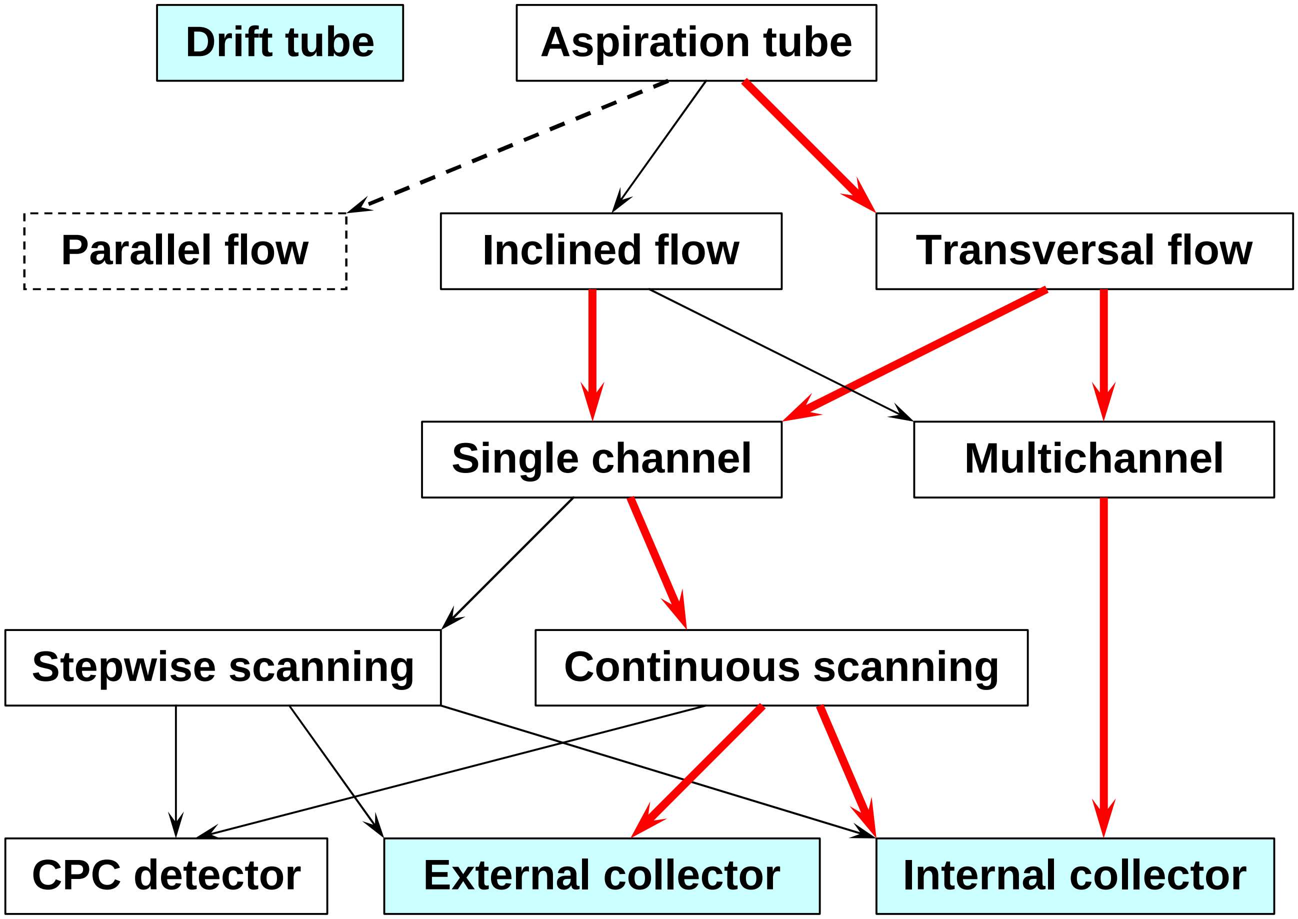
FIGURE 100. Longitudinal section through a Gerdien aspirator.

Large ions..........

CONTEMPORARY METHODS OF MEASUREMENT OF AIR ION MOBILITY DISTRIBUTION

Classification of methods according to:

- **air flow**: drift tube, parallel flow, transversal flow, inclined flow;
- **recording of distribution:** single channel stepwise scanning, single channel continuous scanning, multichannel measurement;
- **particle detection:** CPC detector, external collector electrometer, internal collector electrometer



DRIFT TUBES

A forerunner:

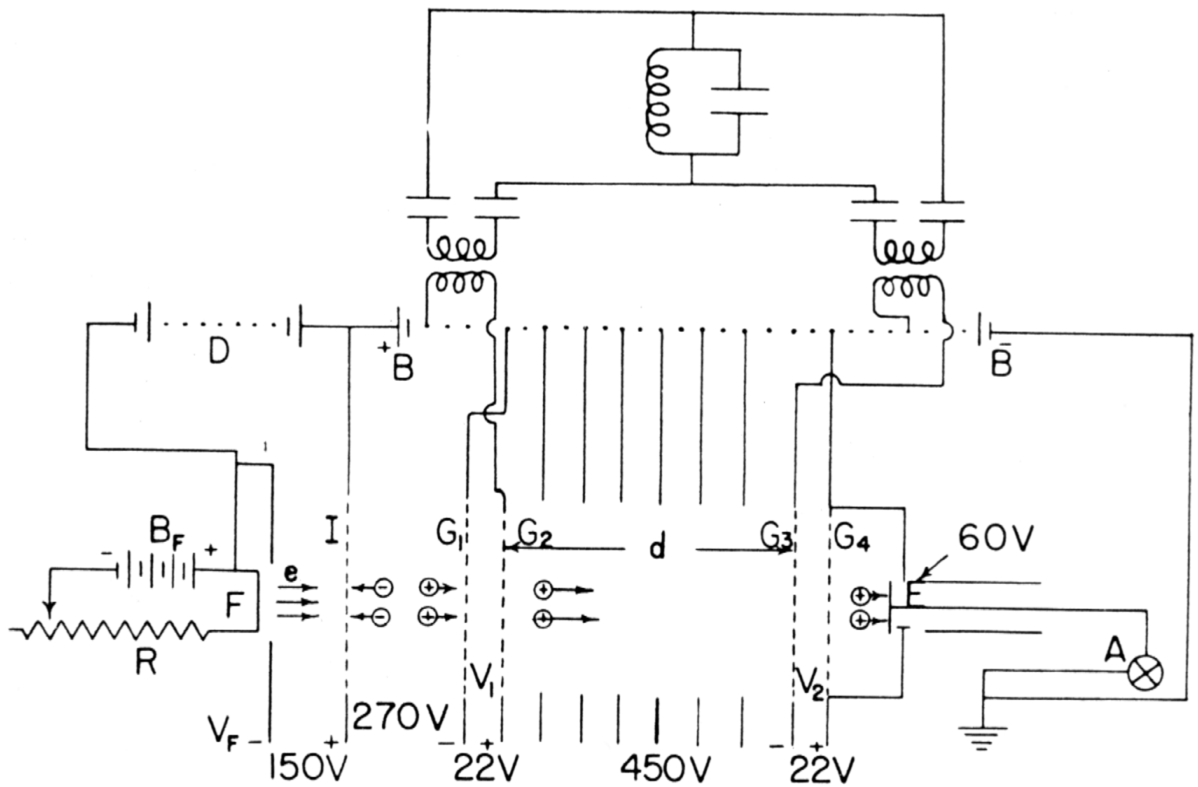


Fig. 1.8. Schematic diagram of the Tyndall-Powell four-gauze shutter method.

J.W. Leonhardt et al.: „A high resolution IMS...", IJIMS 3(2000)1,43-49, p. 44

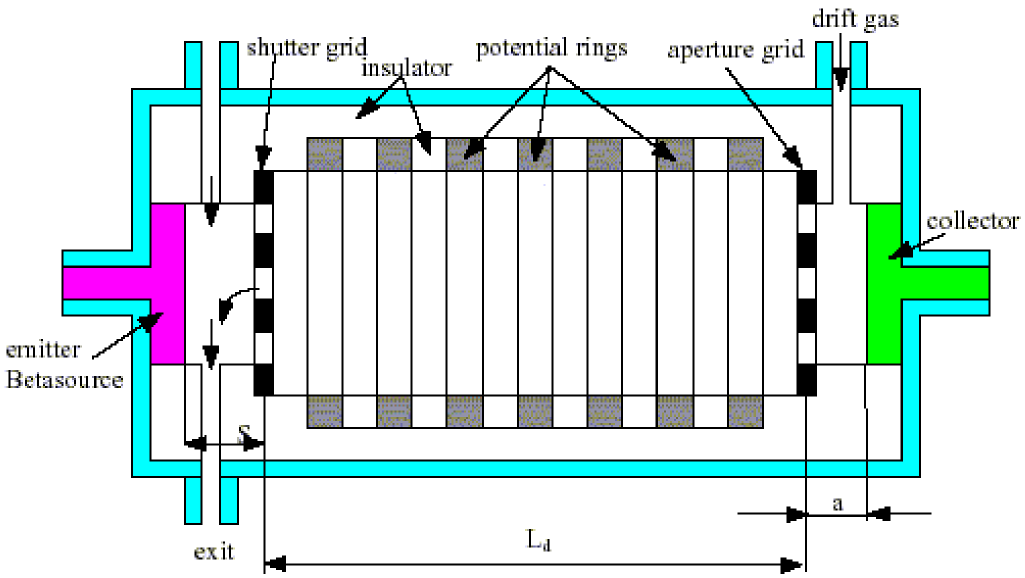


Figure 1: Scheme of an IUT - IM cell

Figure 1:
The Lightweight Chemical Detector

International Journal

for Ion Mobility Spectrometry

INTERNATIONAL SOCIETY for ION MOBILITY SPECTROMETRY

3(2000)1

Official publication of the

International Society for Ion Mobility Spectrometry

Gary Alan Eiceman
Zeev Karpas

ION MOBILITY SPECTROMETRY

CRC

CRC Press
Boca Raton Ann Arbor London Tokyo

INTEGRAL ASPIRATION CONDENSER

$$I = \frac{CV}{\varepsilon_\circ} Zne \quad \& \quad I = \Phi ne \quad \Rightarrow \quad Z_\circ = \frac{\varepsilon_\circ \Phi}{CV}$$

Riecke, E. (1903) Beiträge zu Lehre von der Luftelektrizität. *Ann. Phys*. **12**, 52–84.

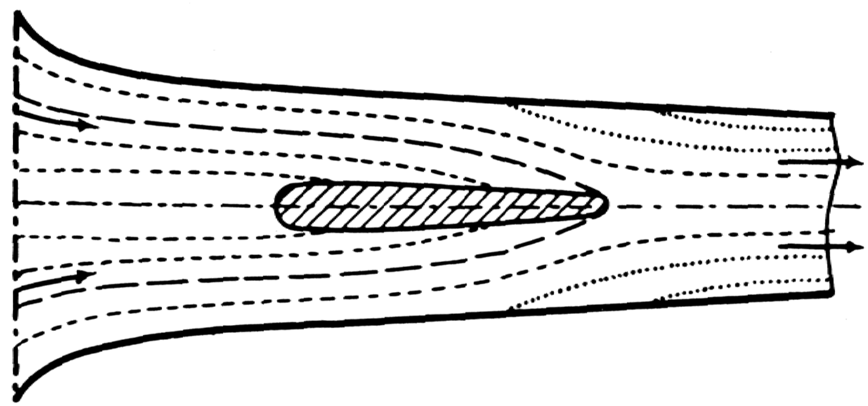


FIGURE 4.1. Flow lines in the measuring capacitor:

- - - - - - flow lines; — — — — boundary surface; · · · · · flow lines on which $\varrho(k) = 0$; — · — · — · — entrance surface.

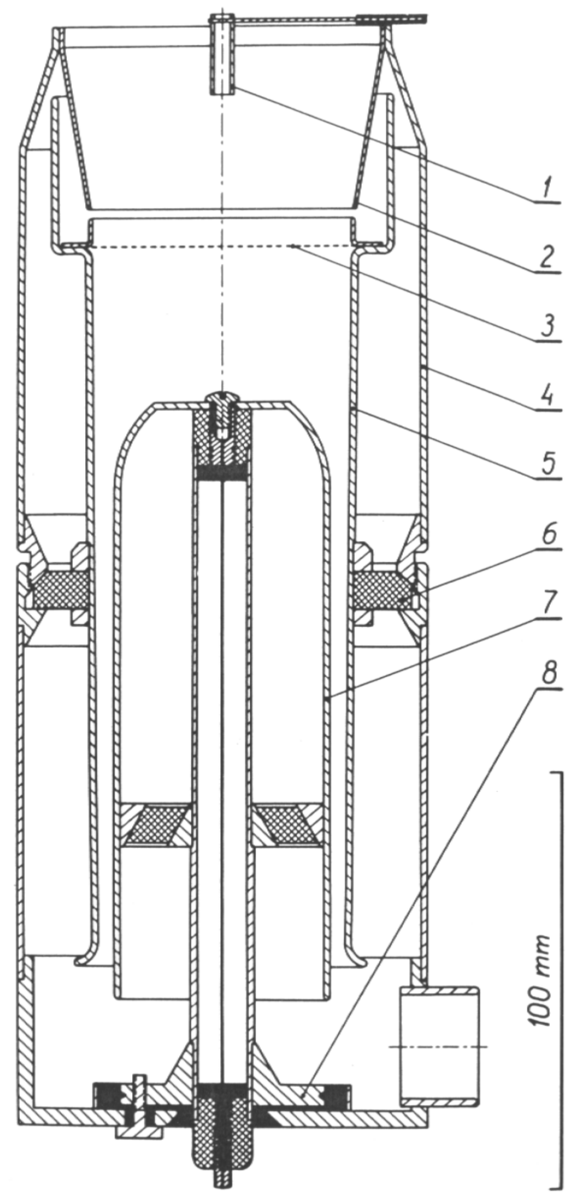


FIGURE 36.1. Measuring capacitor of the SAI-TGU-66 counter.

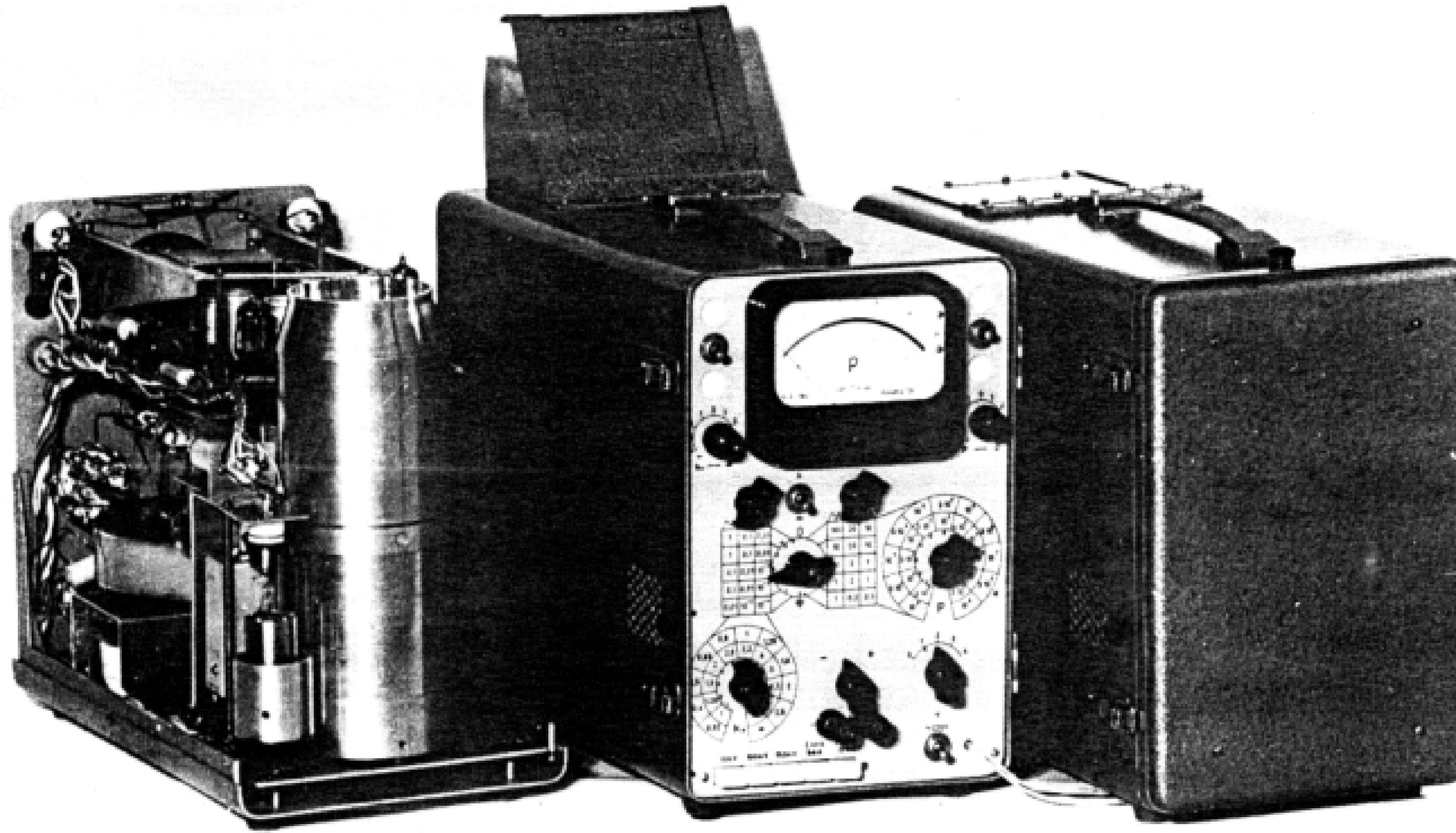
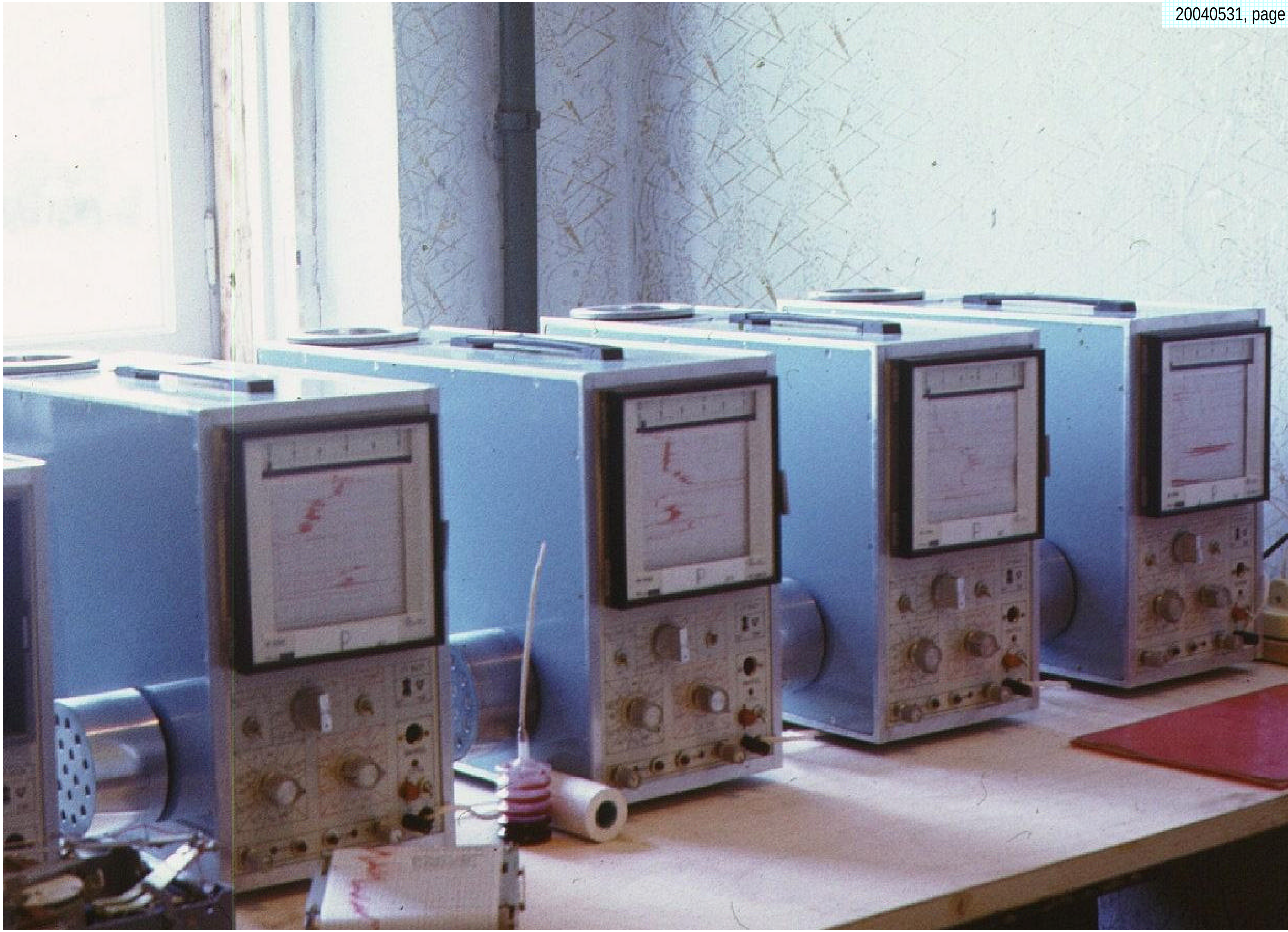
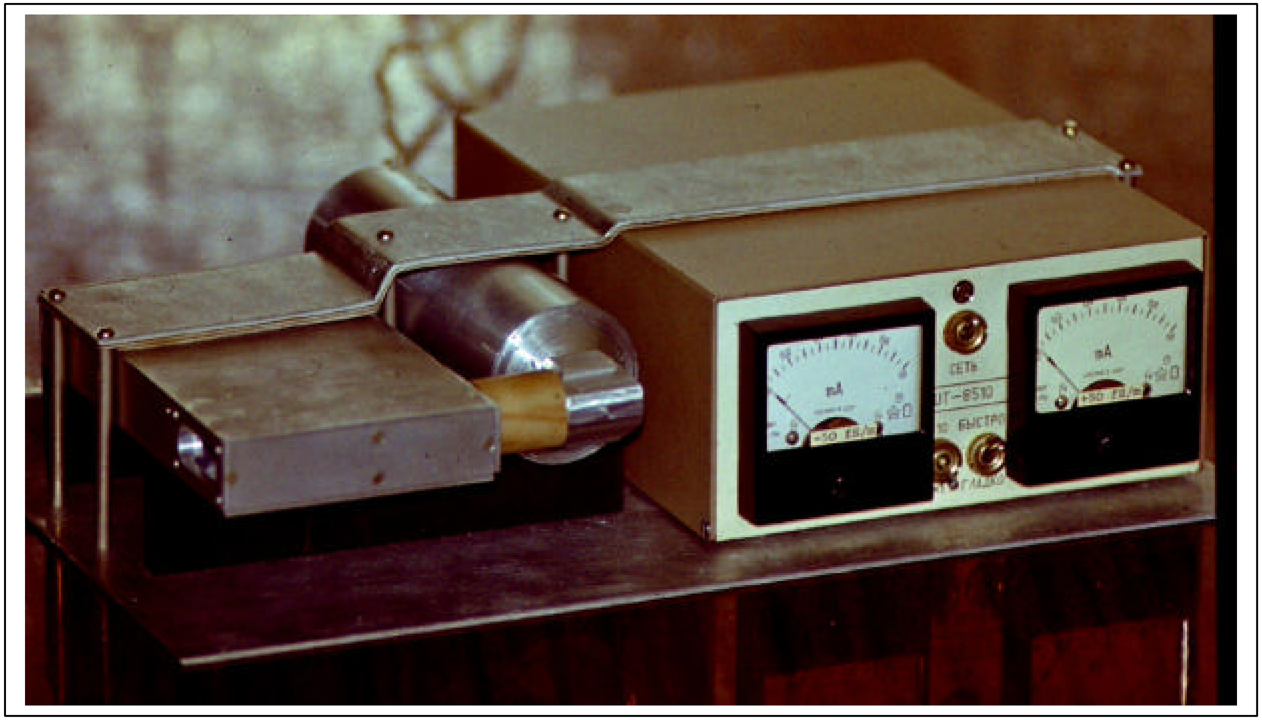
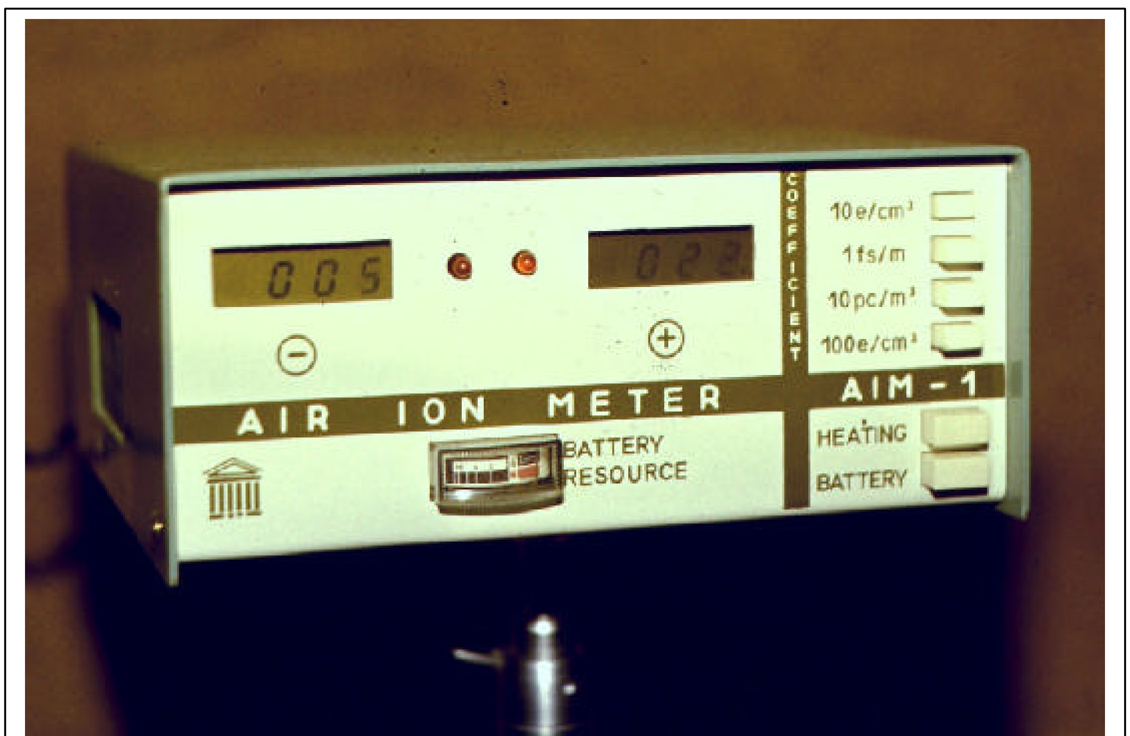


FIGURE 36,5. Three forms of the SAI-TGU-66 counter (with cover removed, in working state, in portable state).






COEFFICIENT
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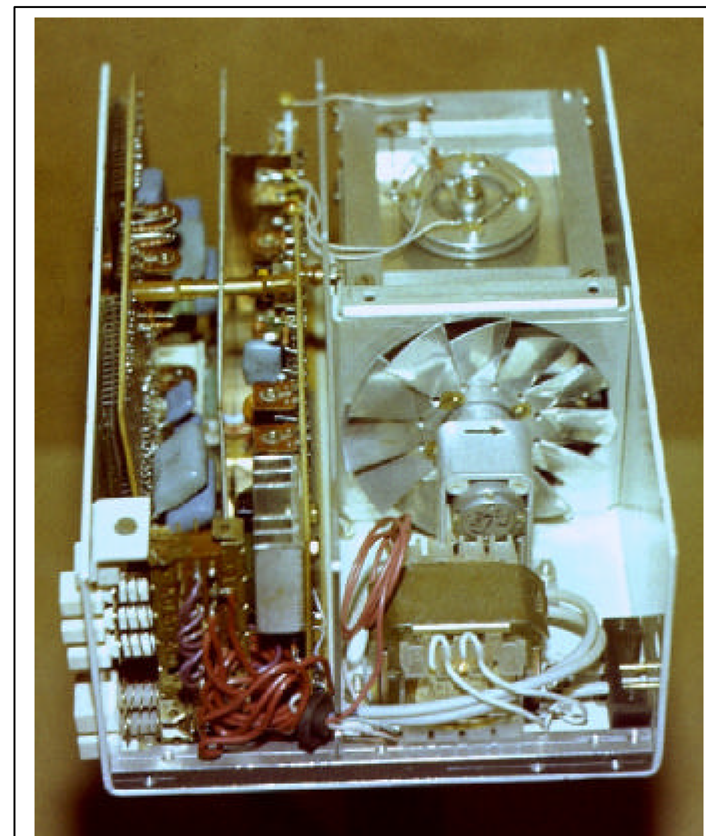
BATTERY RESOURCE



DIFFERENTIAL ASPIRATION CONDENSERS

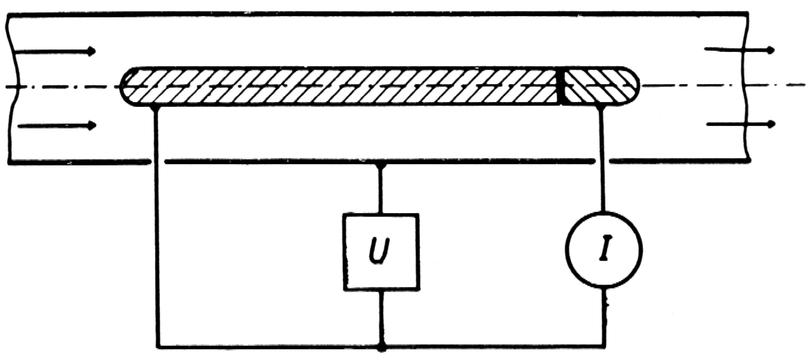


FIGURE 7.1. Differential counter of the first order with a divided electrode.

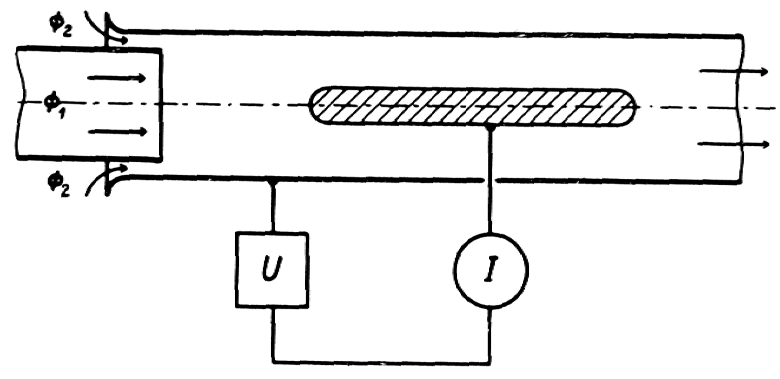


FIGURE 7.3. Differential counter of the first order with a divided air flow.

DMA

MULTICHANNEL ASPIRATION CONDENSER

YUNKER

Results

Preliminary measurements using an electrometer of sensitivity 2000 mm per volt gave, for the natural positive ions, a mobility-spectrum such as shown in Figure 2. It is seen to include a band of mobilities between

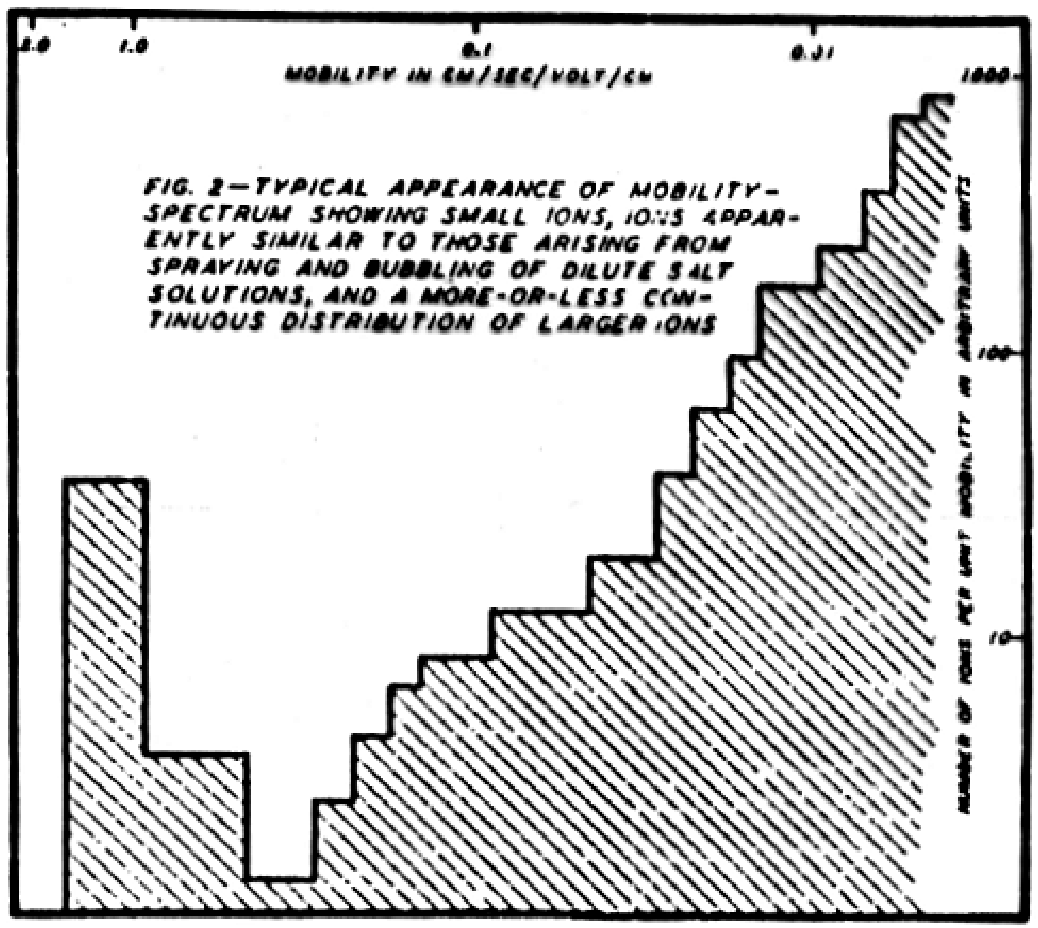


FIG. 2—TYPICAL APPEARANCE OF MOBILITY-SPECTRUM SHOWING SMALL IONS, IONS APPARENTLY SIMILAR TO THOSE ARISING FROM SPRAYING AND BUBBLING OF DILUTE SALT SOLUTIONS, AND A MORE-OR-LESS CONTINUOUS DISTRIBUTION OF LARGER IONS

FIRST MULTICHANNEL MOBILITY ANALYZER OF TARTU UNIVERSITY

Tammet, H.F., Jakobson, A.F. and Salm, J.J. (1973) Multi-channel automatic air ion spectrometer (in Russian). ***Acta Comm. Univ. Tartu*** 320**, 48–75.**

TARTU RIIKLIKU ÜLIKOOLI TOIMETISED

УЧЕНЫЕ ЗАПИСКИ

ТАРТУСКОГО ГОСУДАРСТВЕННОГО УНИВЕРСИТЕТА

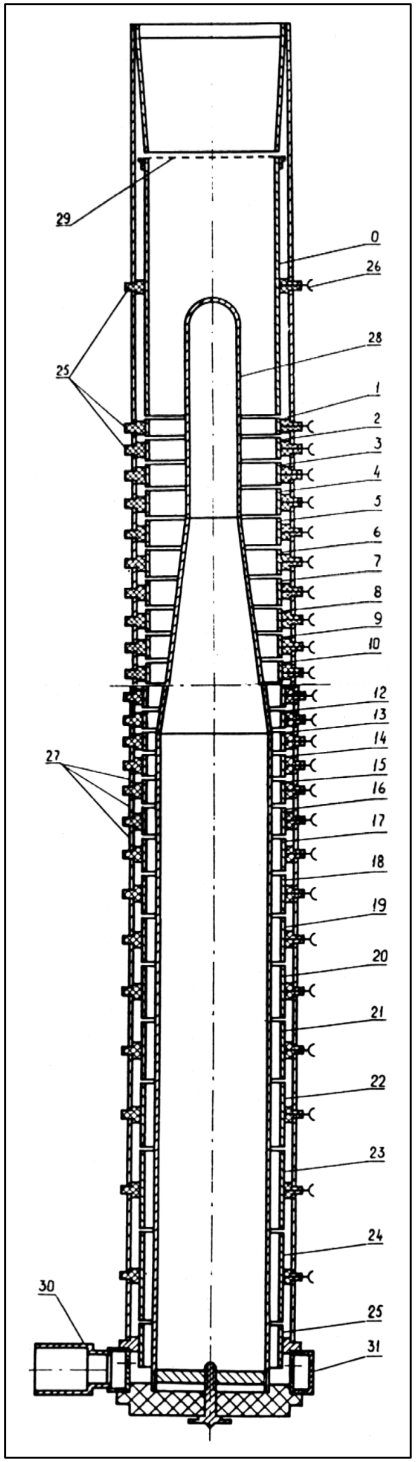
ACTA ET COMMENTATIONES UNIVERSITATIS TARTUENSIS

ALUSTATUD 1893.a Vihik 320 Выпуск ОСНОВАНЫ В 1893.г.

TARTU 1973 pp. 48 – 75

MULTICHANNEL AUTOMATIC SPECTROMETER OF AIR IONS

H. Tammet, A. Jakobson and J. Salm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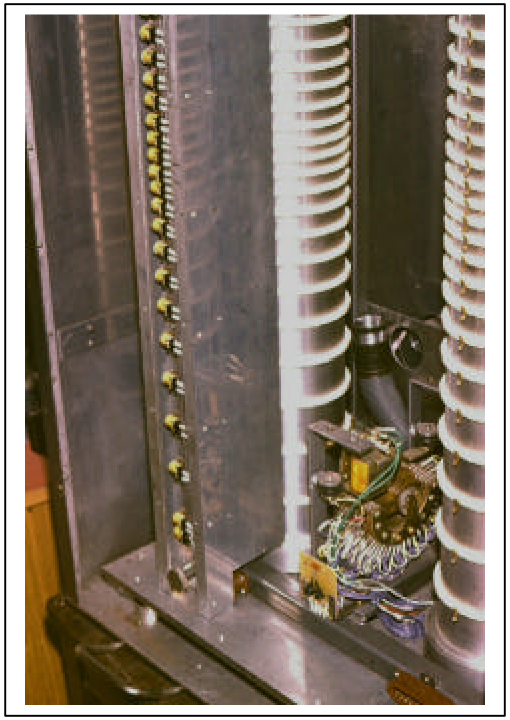
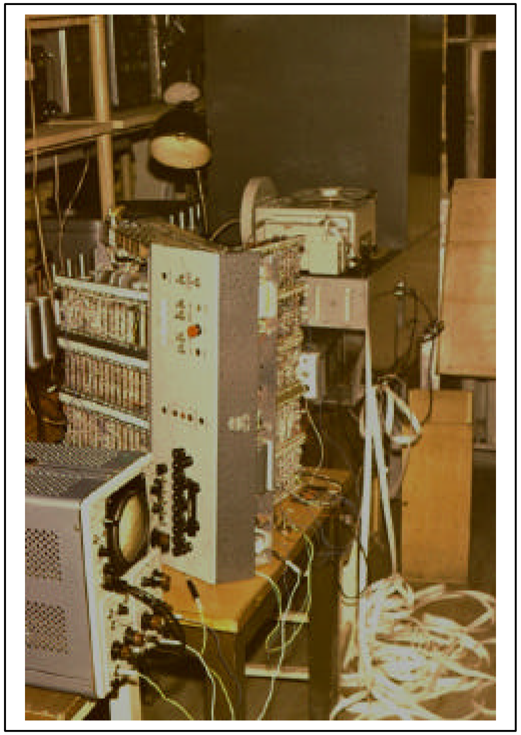
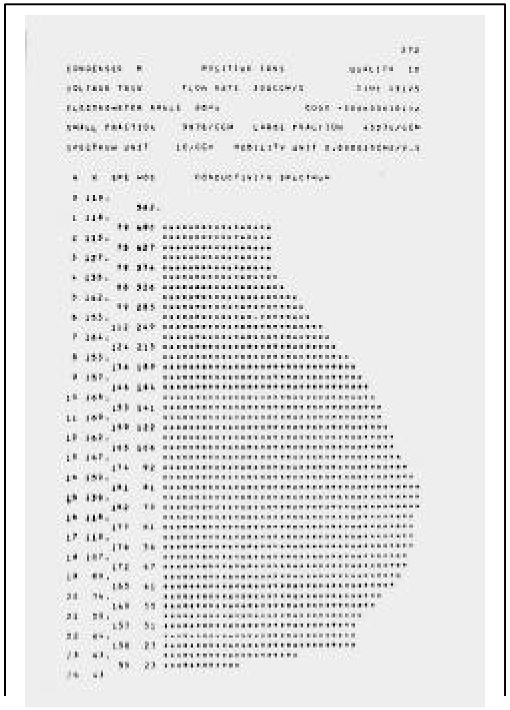
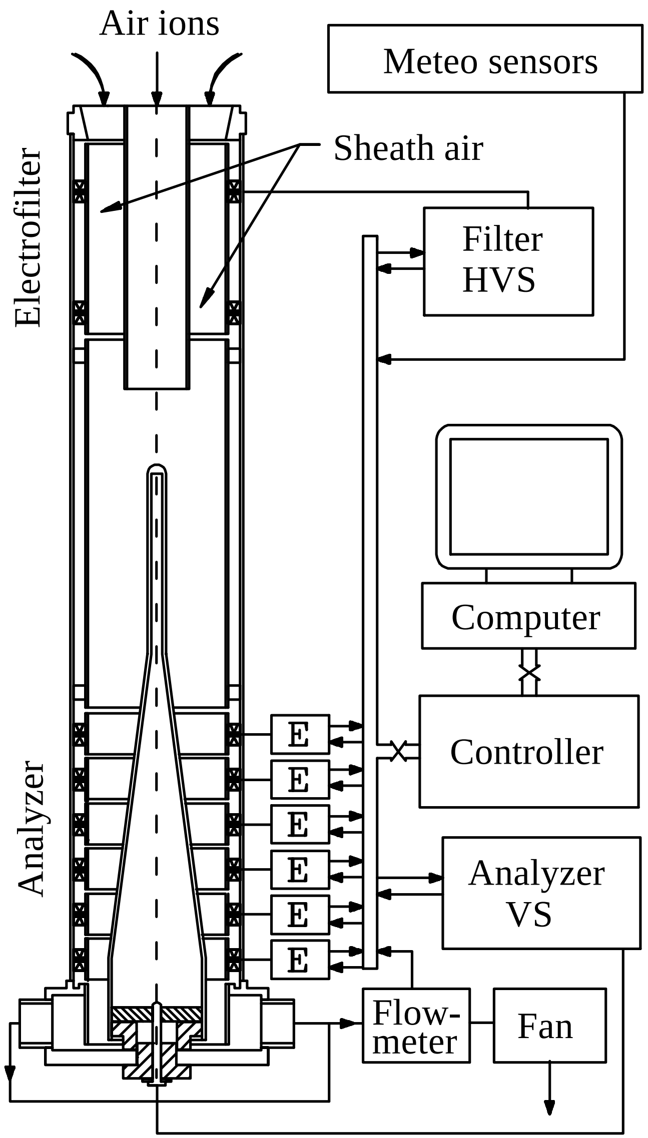
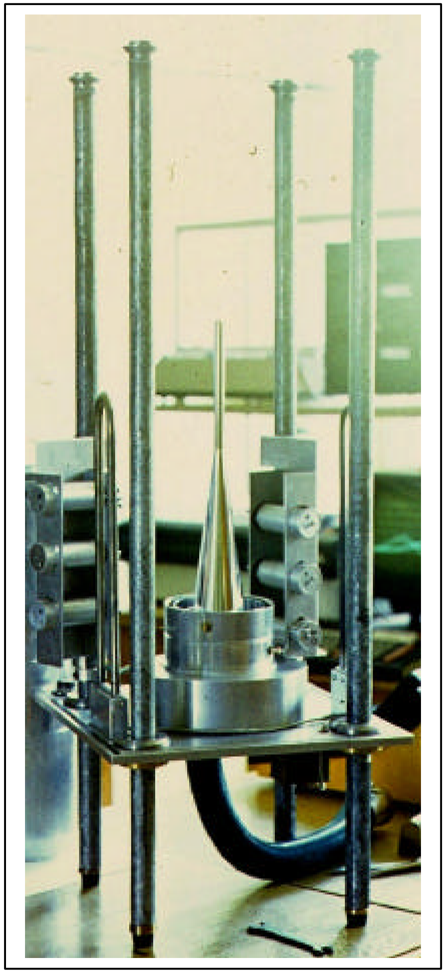


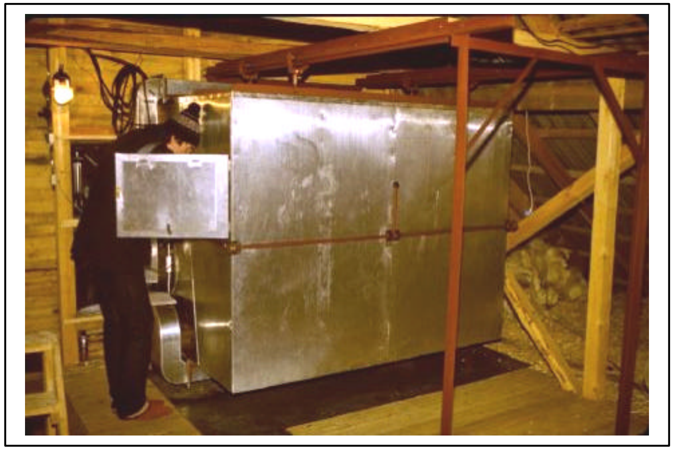



POSITIVE IONS
FLOW RATE
SMALL FRACTION
LARGE FRACTION
MOBILITY UNIT
CONDUCTIVITY SPECTRUM

TAHKUSE







Small air ion spectrometer IS_1 and the measuring system. External dimensions of the spectrometer: height 695 mm, diameter 122 mm.

NEXT GENERATION (developed via EAS)

AIS

Is to be presented by Aadu Mirme

SINGLE-CHANNEL SCANNERS

Tammet, H.F., Hilpus, A.O., Salm, J.J. and Üts, E.J. (1977) An air ion spectrometer for the detection of some admicture in air (in Russian). *Acta Comm. Univ. Tartu* **409**, 84–88.

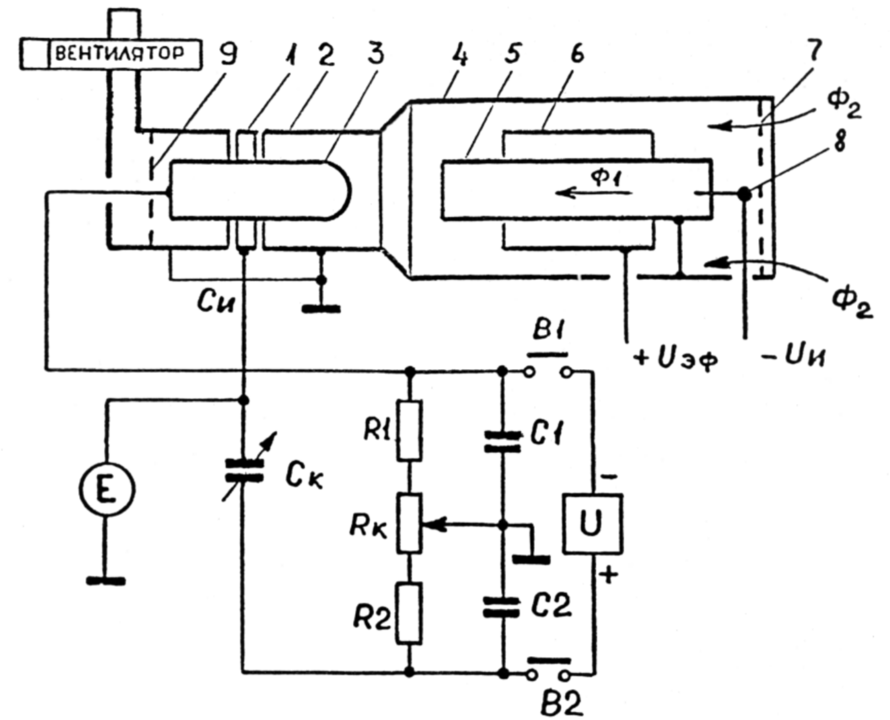
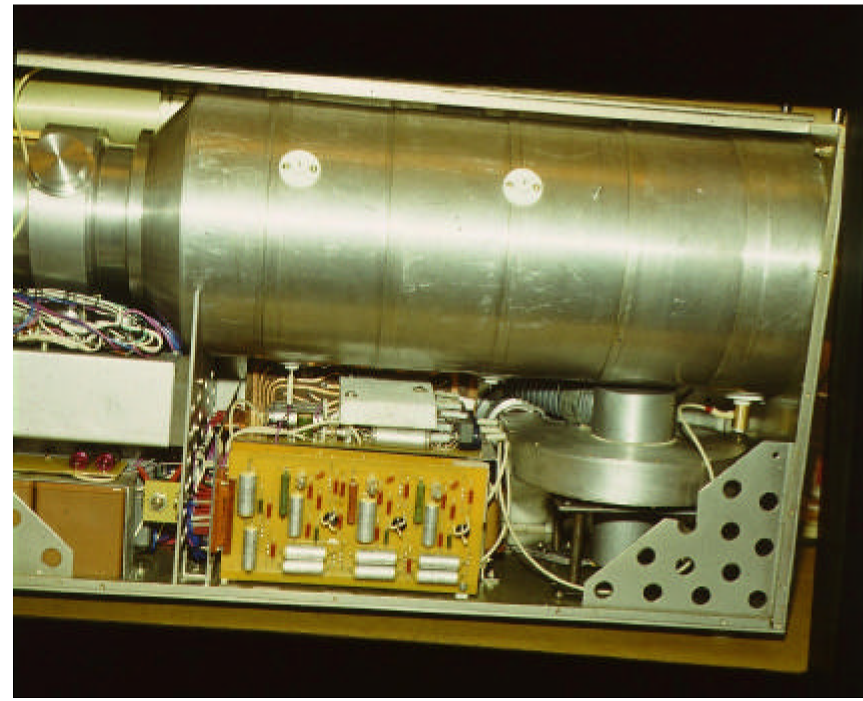


Рис.2. Функциональная блок-схема спектрометра аэроионов.

85



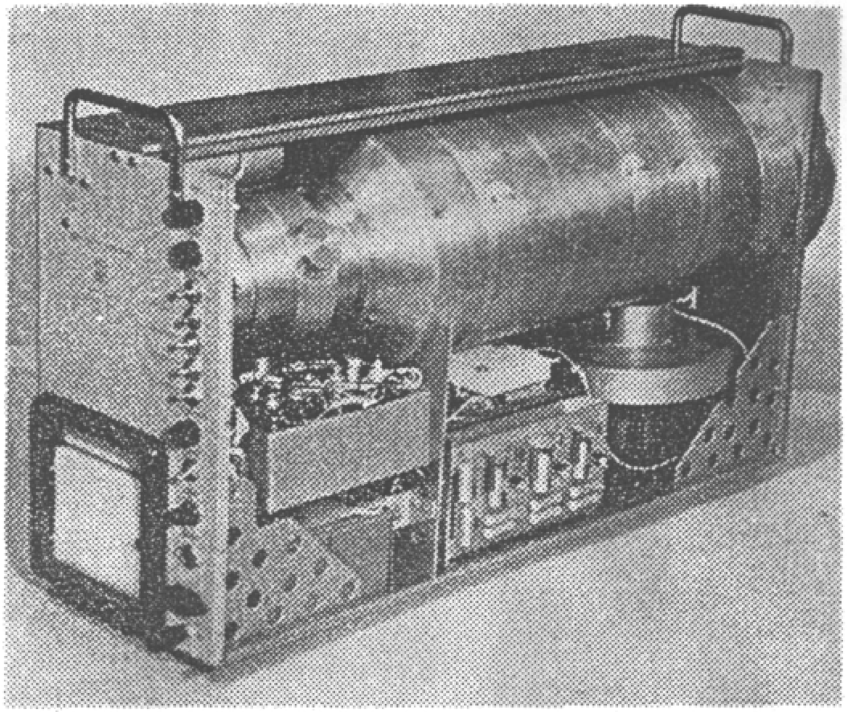
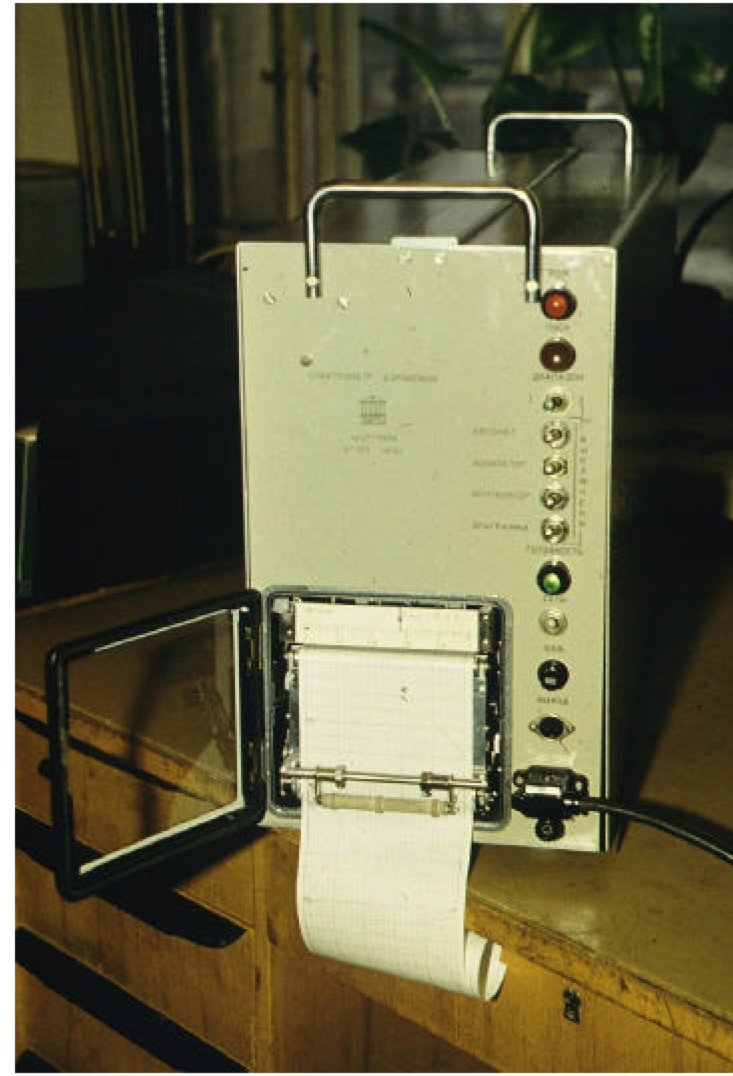


Рис. I. Спектрометр аэроионов UT-7509 со снятым кожухом.
Принцип работы спектрометра поясняет рис. 2.



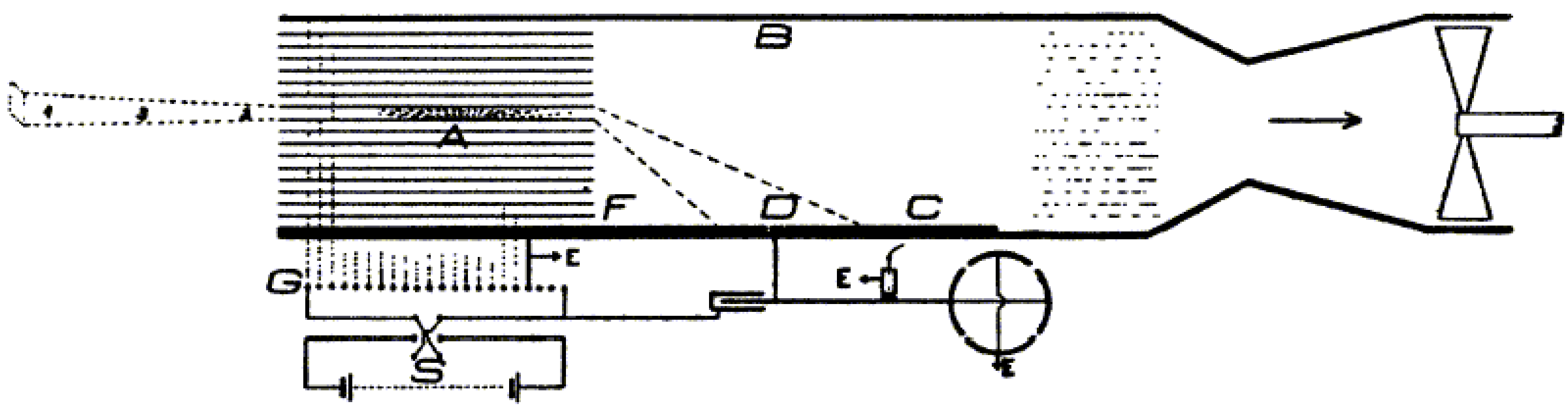
ERIKSON TUBE

THE CHANGE OF MOBILITY OF THE POSITIVE ION IN AIR WITH AGE.

BY HENRY A. ERIKSON.

AT the December, 1920, meeting[1] of the American Physical Society, the writer reported results indicating that there is very little difference in the mobility of the positive and negative ions in air if the mobility is measured. immediately after the ions are formed but that after an interval of the order of a second the mobilities assume the normal difference giving a ratio of 1.4.

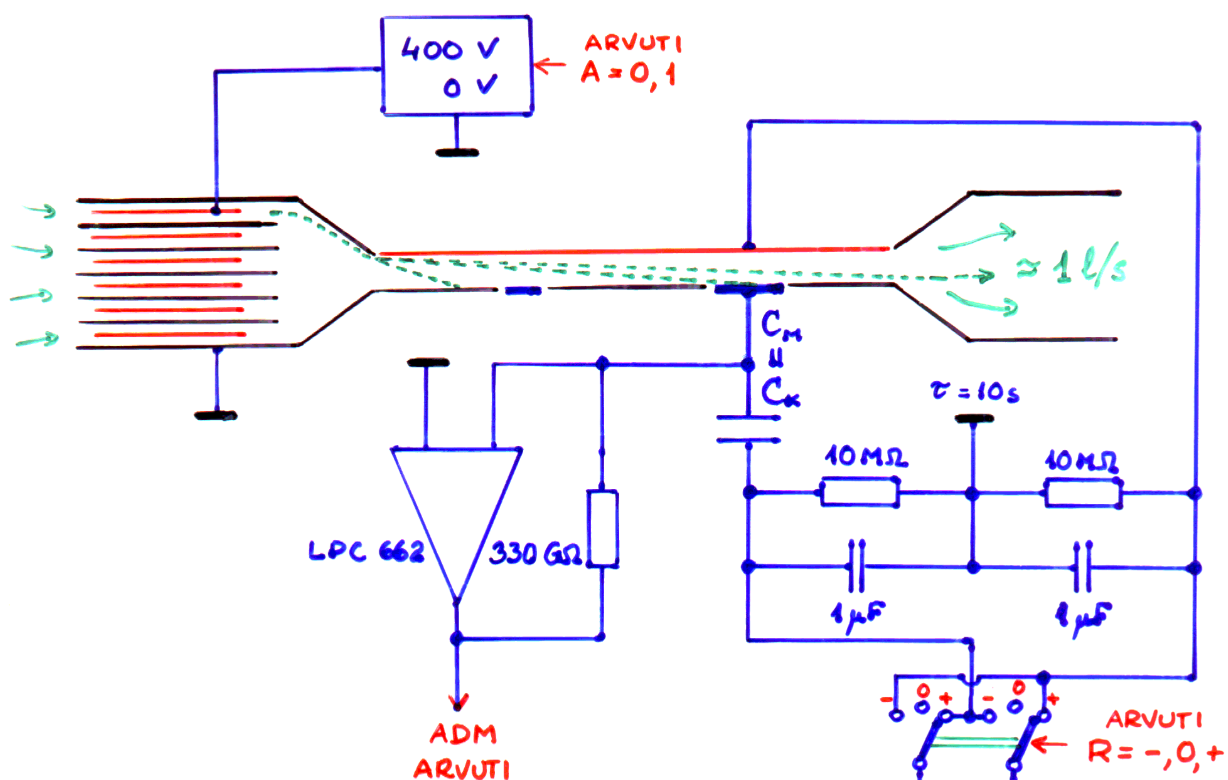
The following is a report of the results oi a further investigation of this effect.



(1921) *Phys. Rev.* **18**, 100–101.


TARTU
UT-9105
SPECTROMETER
MADE IN ESTONIA

UT - 9105

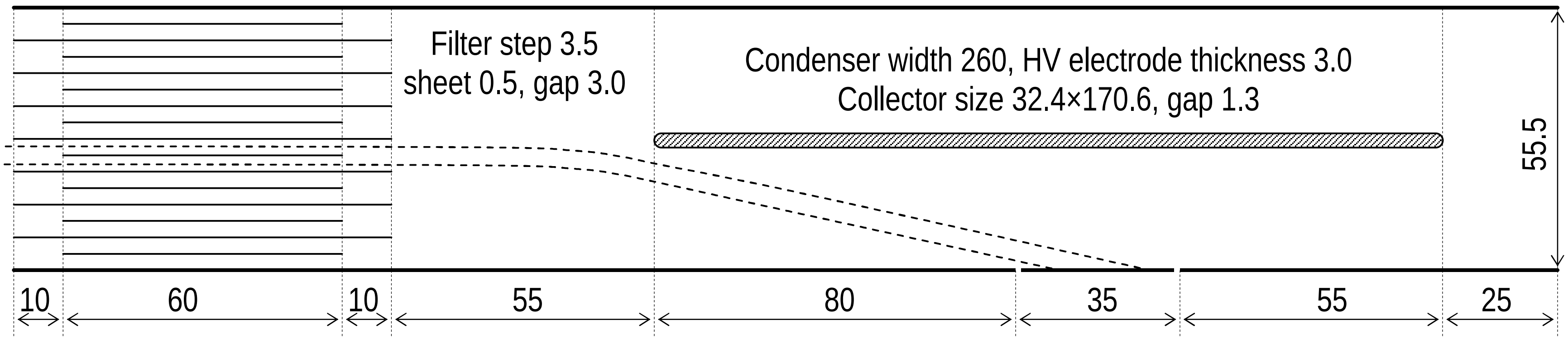


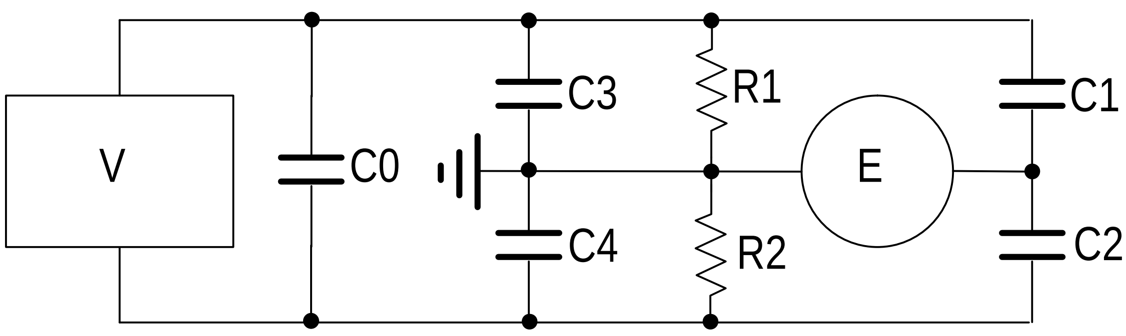
Juhtimiskoodid: 0/16 = ava kinni/lahti

64/96/32 = relee −/0/+

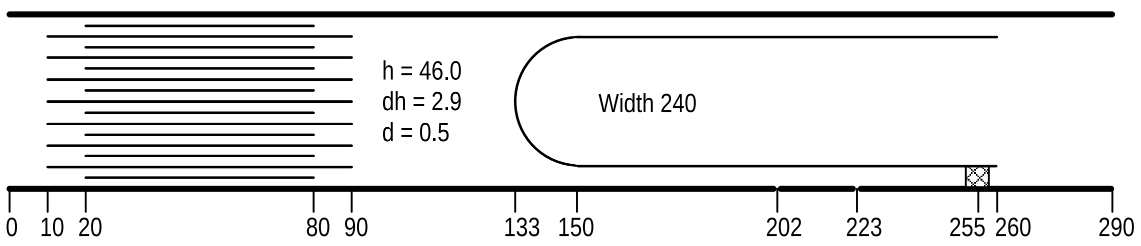
0/128 = pingeallikas välja/sisse

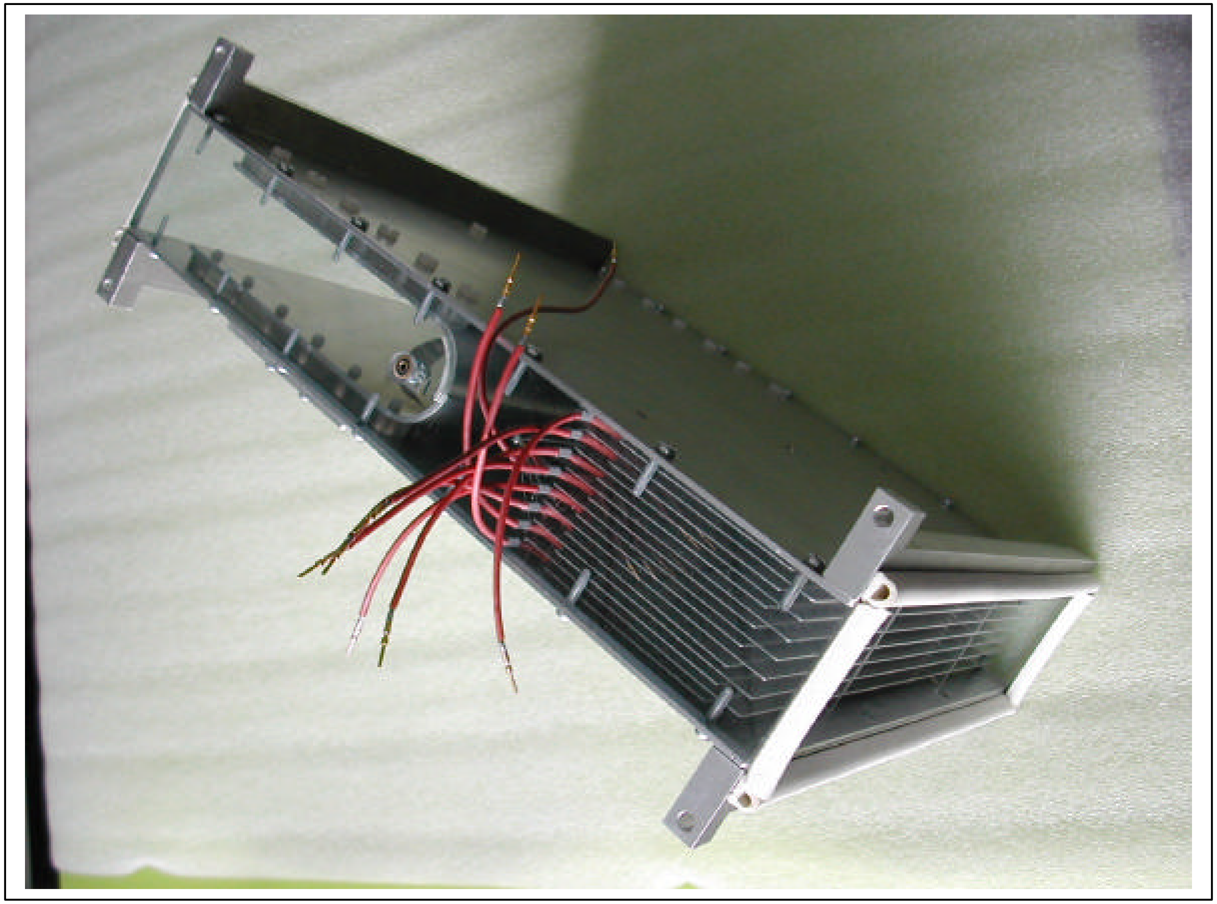
BSMA: Balanced Scanning Mobility Analyzer





BSMA2





Turbo Pascal 7.0

BSMA2D version HT20040402 — scanning mobility distribution

Parameter	Values of parameters ...				
Time HH:MM	23:59	00:00	00:01	00:02	00:03
T : C	21.4	21.4	21.4	21.4	21.4
RH : %	50.2	50.2	50.2	50.2	50.2
p : mb	1021.6	1021.6	1021.6	1021.6	1021.6
+- noise -+	+ 2 -	+ 2 -	+ 2 -	+ 3 -	+ 2 -

Mobility↓	Mobility fraction concentrations cm-3 ...									
0.018-0.024	45	91	54	95	51	92	47	99	55	89
0.024-0.032	43	81	43	85	40	85	41	83	51	78
0.032-0.042	39	62	43	73	40	75	45	68	45	72
0.042-0.056	38	63	38	61	32	58	36	61	36	59
0.056-0.075	32	53	28	51	30	48	31	51	30	52
0.075-0.100	22	46	24	44	23	44	21	46	23	44
0.100-0.133	18	45	21	43	27	34	21	38	20	39
0.133-0.178	16	30	16	26	13	33	18	22	12	28
0.178-0.237	10	25	10	20	14	17	12	22	6	23
0.237-0.316	8	6	5	6	6	9	4	10	2	9
0.316-0.422	-0	5	1	4	1	3	-1	2	-3	10
0.422-0.562	0	9	1	4	3	6	-1	6	3	0
0.562-0.750	65	12	68	11	68	12	70	10	69	8
0.750-1.000	117	17	122	16	122	20	123	21	123	20
1.000-1.334	200	98	198	103	202	96	200	101	198	98
1.334-1.778	119	203	120	205	117	192	123	203	123	196
1.778-2.371	27	151	31	149	31	152	32	150	28	153
2.371-3.162	-3	45	2	47	5	50	-2	49	-2	52

Diameter↓	Size fraction concentrations cm-3 ...									
0.40-0.63	22	185	31	185	34	191	28	189	24	194
0.63-1.00	273	289	274	294	274	277	278	291	277	282
1.00-1.58	230	56	237	53	239	57	240	57	240	51
1.58-2.51	11	24	9	18	13	21	6	22	2	26
2.51-3.98	41	93	46	84	50	80	48	76	37	84
3.98-6.31	86	152	85	147	80	141	82	149	84	147
6.31-10.0	123	225	135	243	125	242	129	239	145	230
n-cluster	525	526	541	531	546	522	546	535	540	528
Z-cluster	1.15	1.67	1.17	1.68	1.18	1.69	1.16	1.68	1.15	1.70
d-particle	6.0	5.8	6.0	6.0	5.9	6.0	6.0	6.0	6.3	5.9

```
 Scan  16+      -28   -21   -17   -20   -18   -18   -19   -20   -19
 00:04:31       -21   -22   -21    -7     5    20_
Balance: manual 54%, automatic 67%;   Power 23.7 V;   Electrometer bias -0.2 mV
Diurnal files on (Ctrl+M turns off)                              EXIT = Ctrl+X
```

DIFFUSION LIMIT OF RESOLVING POWER

JULY 15, 1929 PHYSICAL REVIEW VOLUME 34

THE DISTRIBUTION OF MOBILITIES OF IONS IN MOIST AIR*

BY JOHN ZELENY
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(Received March 22, 1929)

ABSTRACT

A search was made in undried air for groups of ions having different mobilities and no such distinct groups were found among ions two or more seconds after their formation. A critical study was made of the effects of diffusion upon the distribution of ions moving in an electric field. Experimental results obtained for N, the volume density of ions which after a time t are located at a distance r from the origin agree fairly well with the theoretical formula

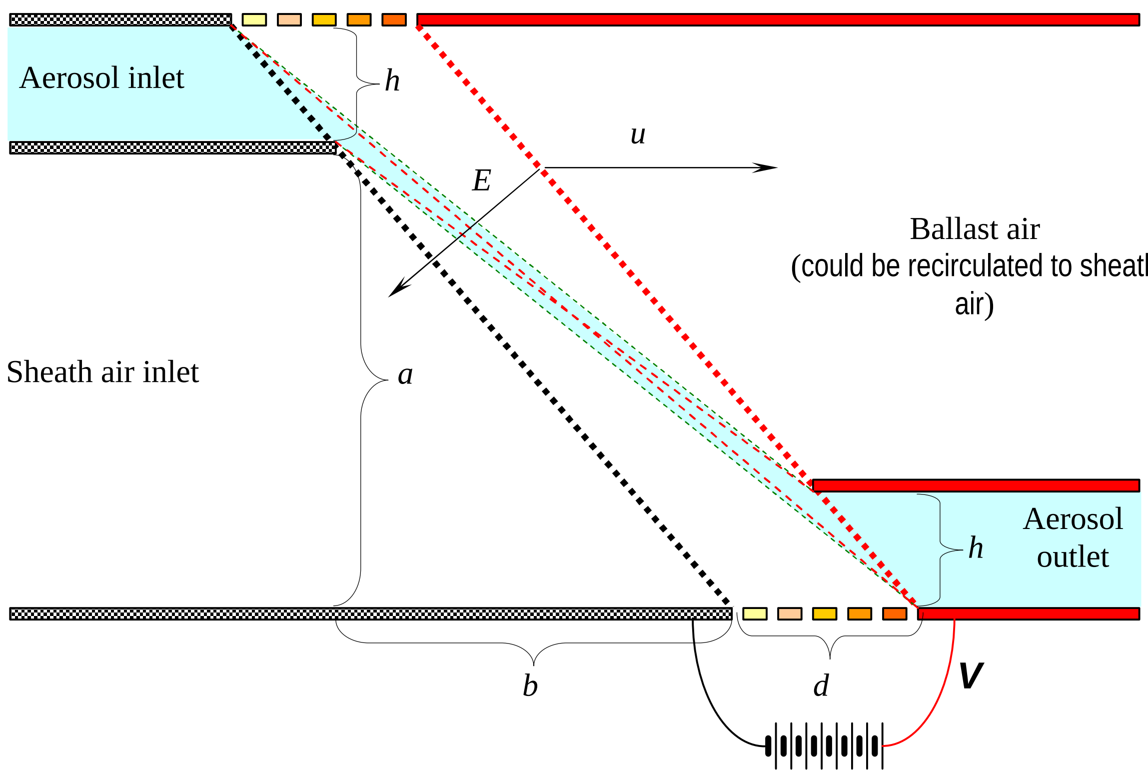
$$N = \frac{N_0}{(4\pi Dt)^{3/2}} e^{-r^2/4Dt},$$

where D is the coefficient of diffusion. The mobilities and the spreading of the ions were measured by a modification of the author's method in which ions passing between two concentric cylinders under an electric field are simultaneously carried axially by a slow, non-turbulent current of air of known velocity. The ions entered

$$\frac{\sigma_Z}{Z} = \sqrt{\mu \frac{2kT}{eV}}$$

Loscertales, I.G. (1998) Drift differential mobility analyzer, *J. Aerosol Sci.*, ***29***, 1117–1139.

IGMA: Inclined Grid Mobility Analyzer



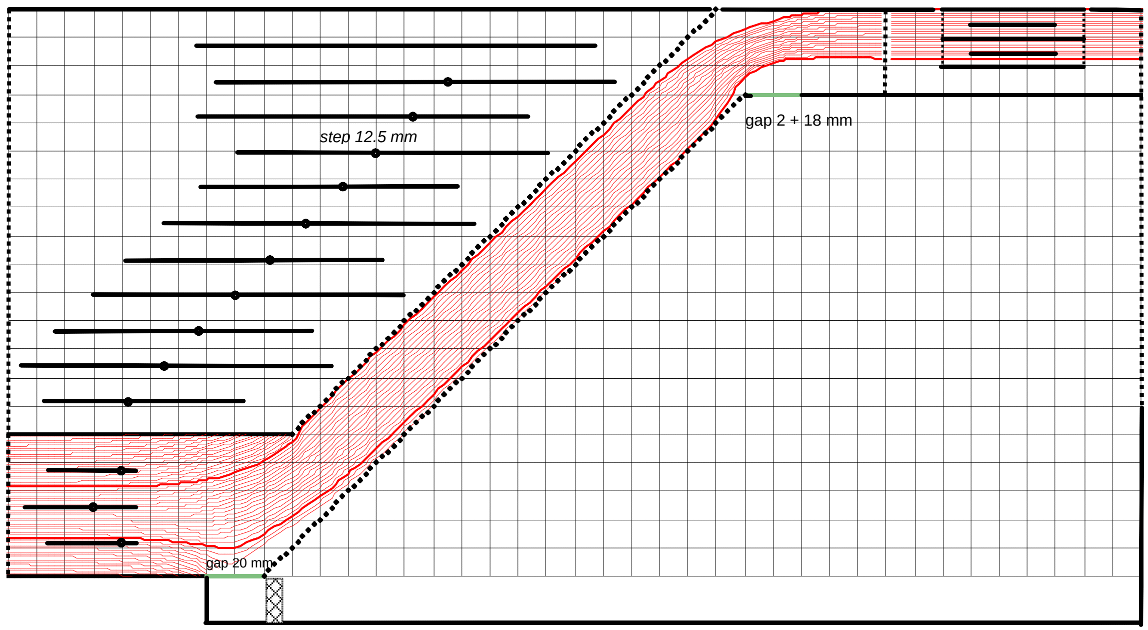
ADVANTAGES AND DISADVANTAGES OF A PLAIN IGMA

Advantages:

- high mobility resolution,
- easy to keep plug air flow in the instrument,
- simple theoretical calculations,
- calculated transfer function could be trusted without comparative calibration.

Disadvantages:

- one of the aerosol inlet or outlet is on high potential,
- loss on charged particles on attracting grid,
- driving voltage is not effectively used because the beam of monomobile particles does not fill the space between grids.



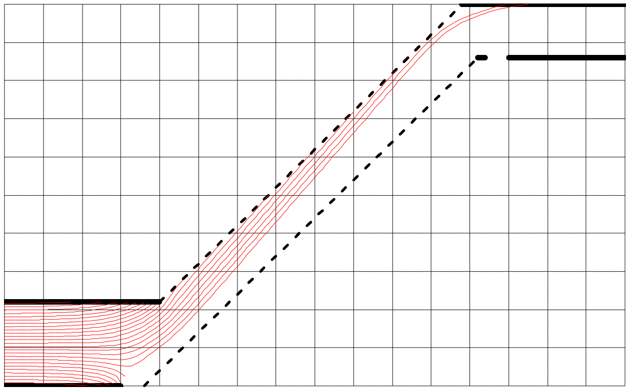
Passage of ions of central mobility in an ideal modified IGMA.

The ions in the outlet are collected by a well-insulated and shielded electrostatic filter powered by an internal battery and DC-DC converter. The collector is connected to the ground through an electrometric amplifier. Electrostatic shielding from the high voltage deflector grid allows free manipulation with mobility control voltage. The deflector grid is connected to a RC circuit with a time constant of about 4 s. The capacitor of this circuit is quickly charged up to 6 kV and slowly discharged through the resistor with a period of 20 s. This assures the logarithmical scanning of mobility from the lowest to the highest value of the mobility range during the 20 s period.

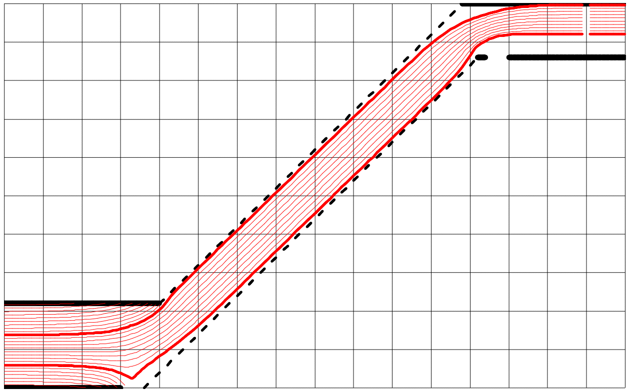
Tammet, H (2003). Method of inclined velocities in the air ion mobility analysis. *Proceedings of the 12th International Conference on Atmospheric Electricity* **1**, Versailles, pp. 399-402.

TRAJECTORIES OF IONS IN A MODIFIED IGMA

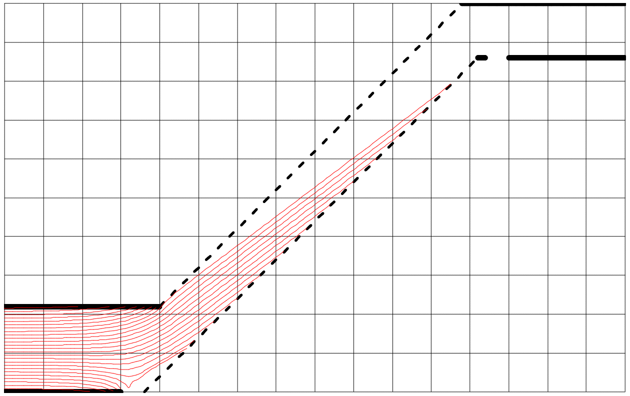
(plug air flow is expected)



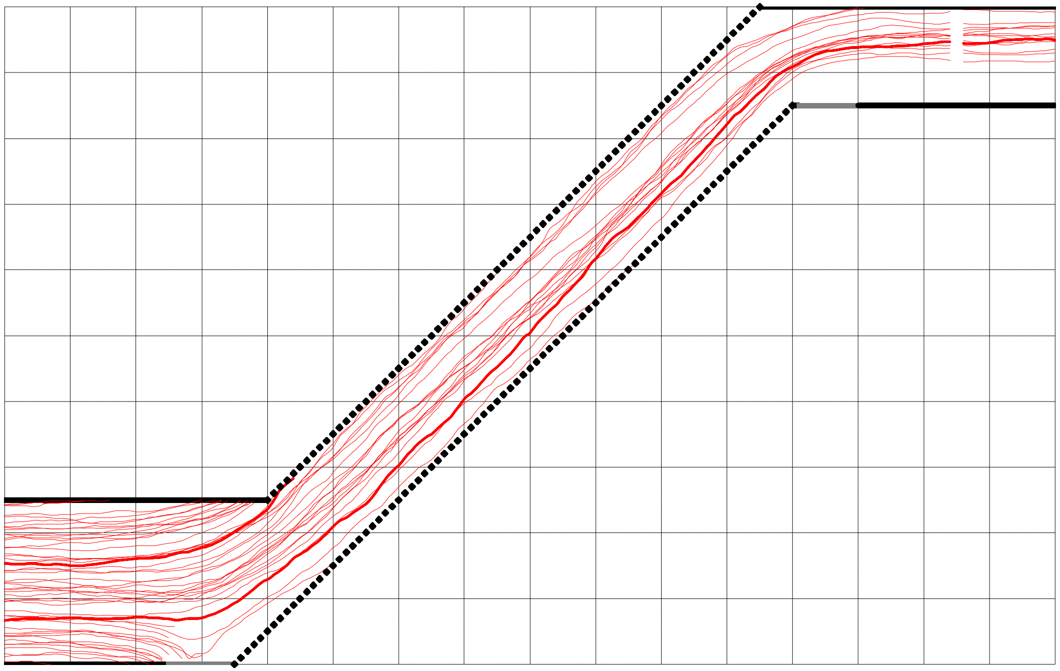
Laminar flow, high mobility



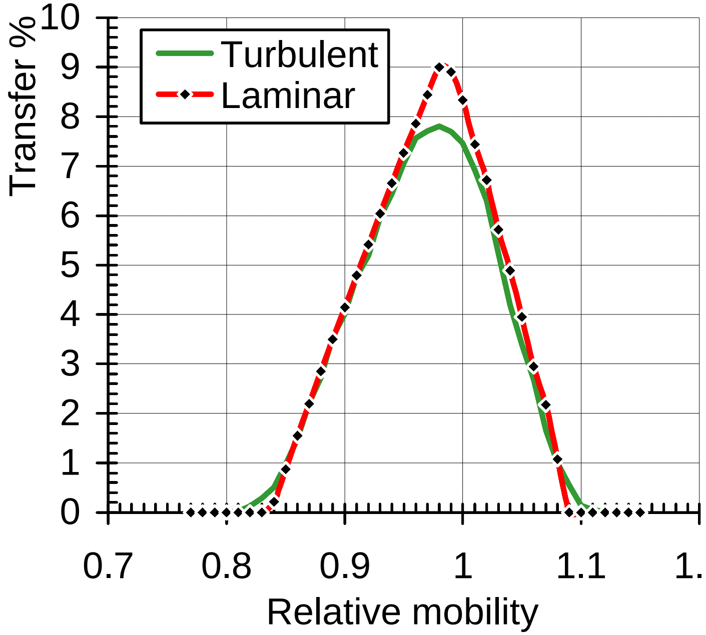
Laminar flow, central mobility



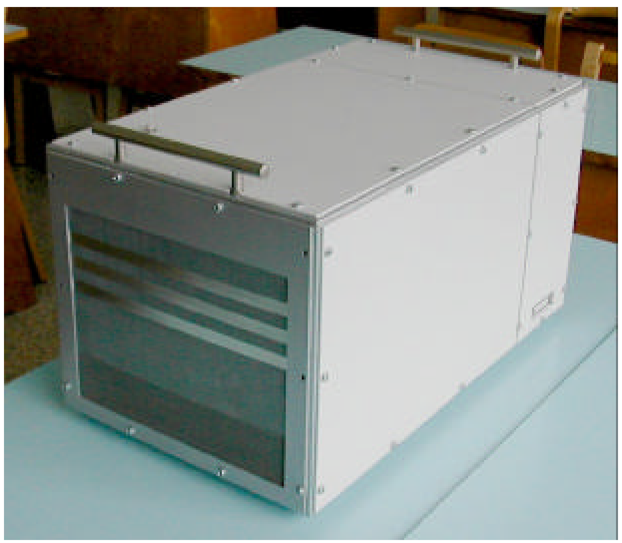
Laminar flow, low mobility

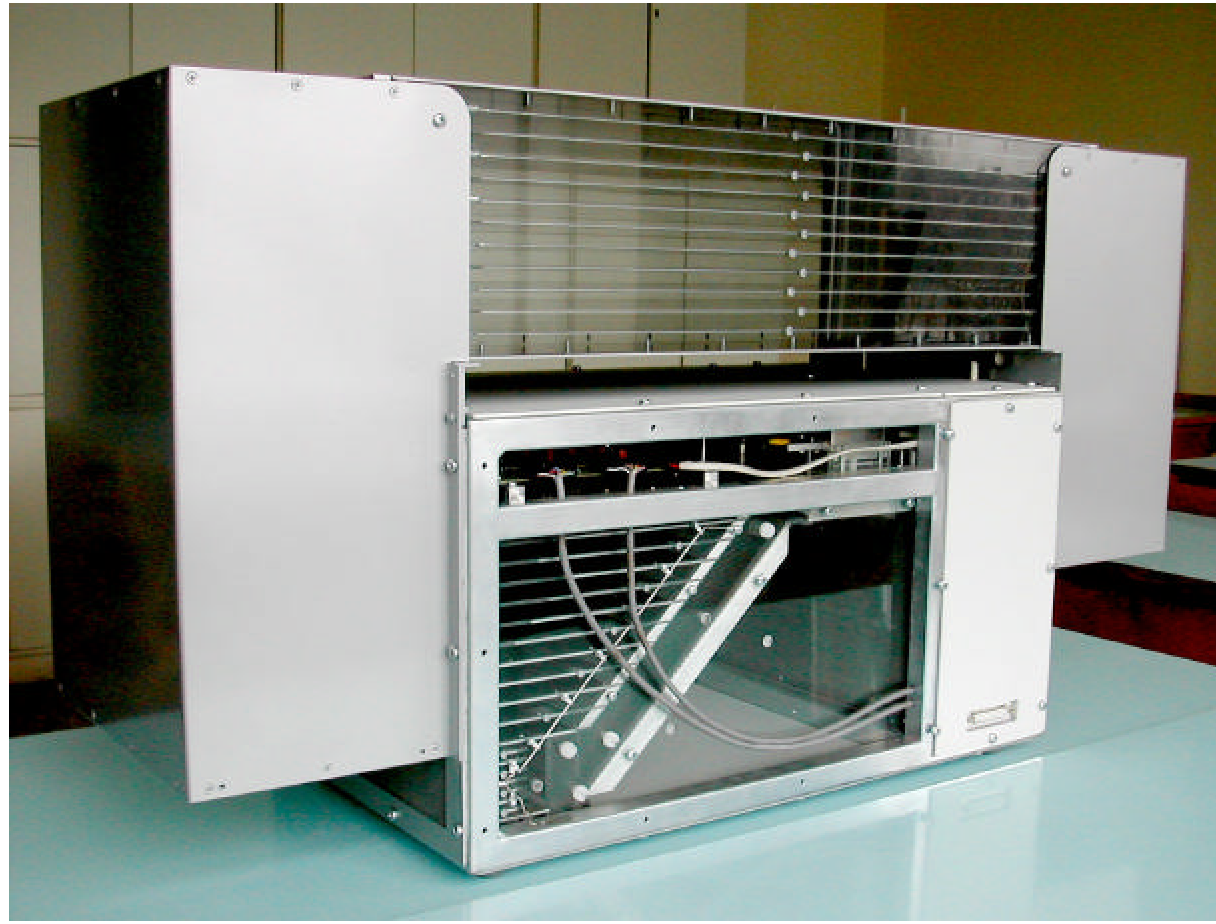


Turbulent flow (e =10%), central mobility.



Transfer functions.





IGMA without the external filter.
Size 53 × 31 × 32 cm, mass 17.5 kg.

IGMA (a side panel off) with the external recirculation filter.
Size 85 × 31 × 48 cm, mass 29 kg.

Pergamon

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A CONDENSATION NUCLEUS COUNTER (CNC) SENSITIVE TO SINGLY CHARGED SUB-NANOMETER PARTICLES

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(*First received* 17 *March* 1999; *and in final form* 24 *September* 1999)

Abstract—The mixing-type particle size magnifier (PSM) of Okuyama *et al.* (1984, *Aerosol. Sci. Technol.* **3**, 353–366) has recently shown an ability to detect positively charged particles with mobility diameters as small as 1.5 nm (Seto *et al.*, 1997, *J. Chem. Phys.* **107**, 1576–1585), well below the sensitivity limit of 2.3 nm available in commercial CNCs. Gamero-Castaño (1999, Ph.D. thesis, Yale University) has shown that the activation of even smaller particles is limited in this PSM by homogeneous nucleation due to cooling of the saturated dibutyl phthalate vapor stream before it mixes with the aerosol. This problem is overcome here by means of a reheater, whereby ions with mobilities (in air) higher than 2 $cm^2 V^{-1} s^{-1}$ can be activated at supersaturations well below the threshold for homogeneous nucleation. The critical supersaturation required to activate ions whose mobility exceeds 0.78 $cm^2 V^{-1} s^{-1}$ (mobility diameter smaller than 1.6 nm) is seen to be independent of size, indicating that this instrument can detect arbitrarily small (charged) particles. The reheater makes it possible also to run the PSM at fairly small vapor flow rates with essentially no vapor loss. Varying the vapor flow rate hence provides a rapid means to scan over the supersaturation in the mixing region, and hence infer the particle diameter (or its charge) with the PSM alone. Coupled to an optical detector this PSM constitutes a condensation nucleus counter (CNC) suitable for the analysis of charged sub-nanometer particles, ions, as well as charged biomolecules and their fragments, with effectively no lower size limit. © 2000 Elsevier Science Ltd. All rights reserved

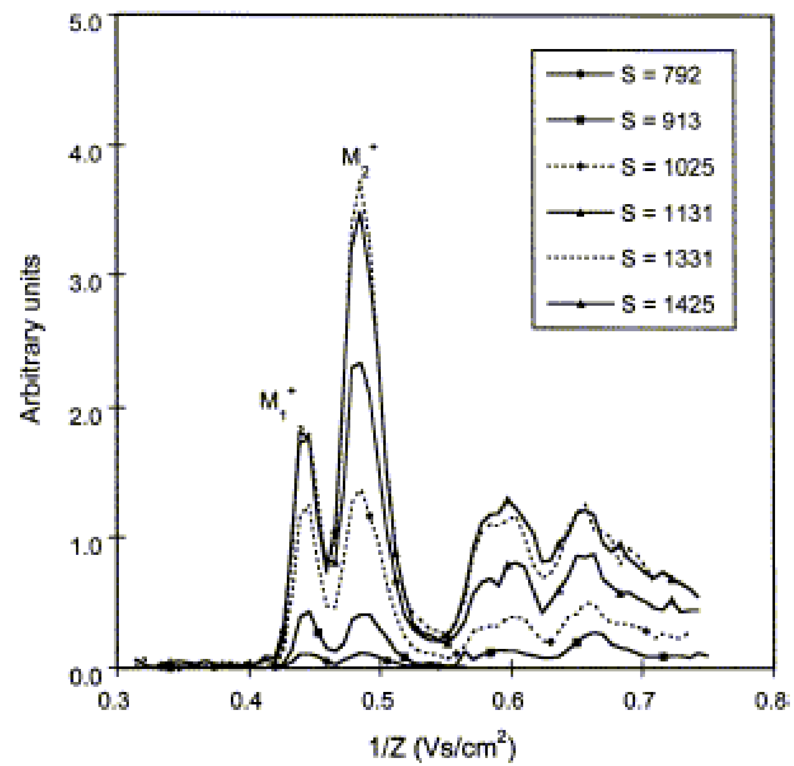

Fig. 5. CNC signal versus inverse mobility for a solution of formamide containing subnanometer ions of tetramethyl ammonium. Each curve is for a different PSM supersaturation. Below a characteristic ion diameter, the supersaturation required to grow ions into micron-drops becomes independent of ion size.