# LABORATORIO DE QUIMICA ANALITICA INSTRUMENTAL I
## Práctica: "Polarografía Clásica"
## Determinación de ácido nalidíxico en tabletas.

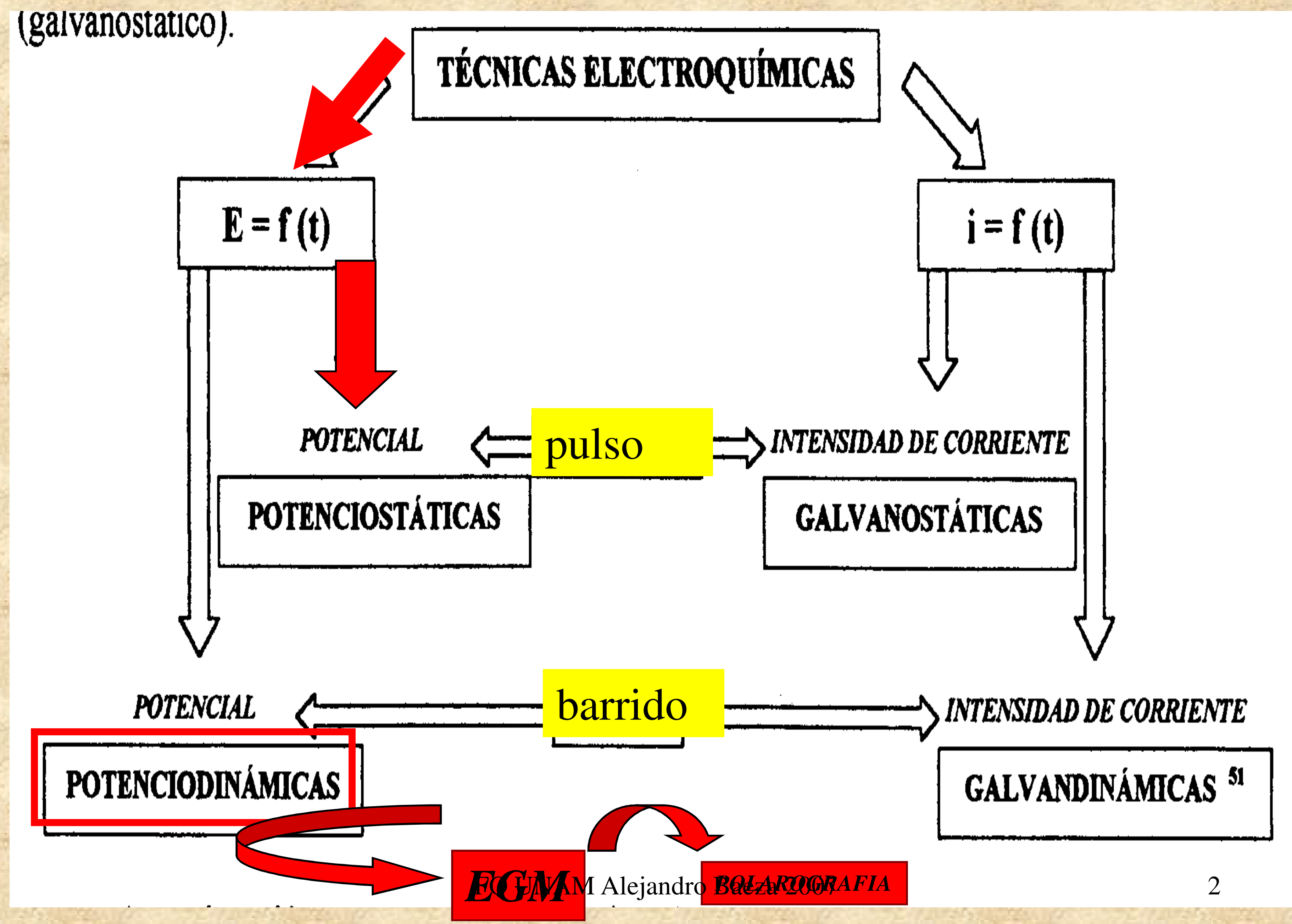
**Objetivos:**

a) Estudiar experimentalmente las condiciones básicas de la polarografía clásica.

b) Determinar el contenido de ácido nalidíxico en un medicamento por medio de una curva de calibración polarográfica con adiciones estándar.

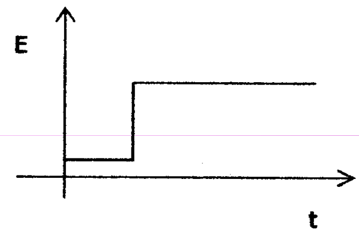
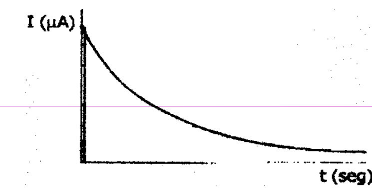
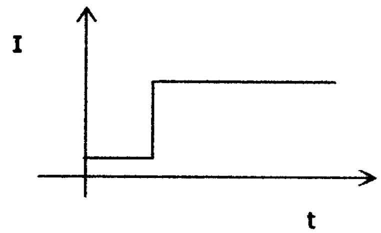
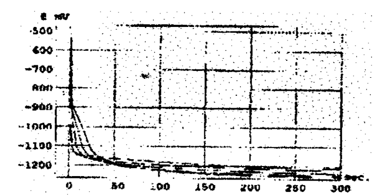
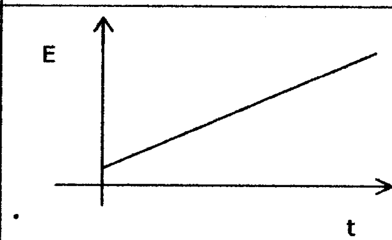
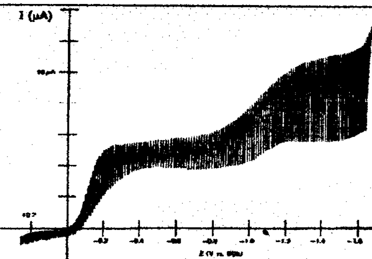
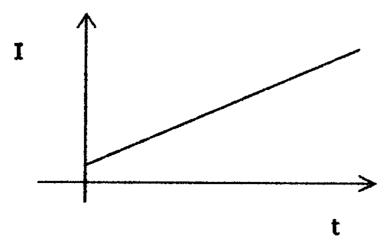
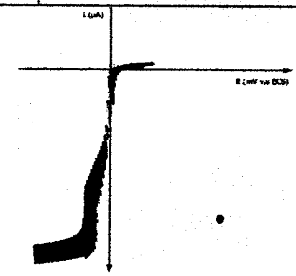
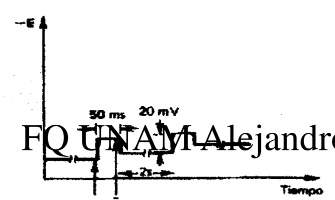
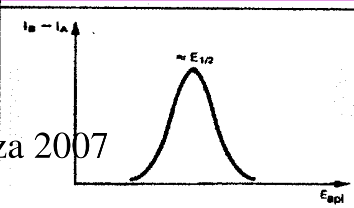


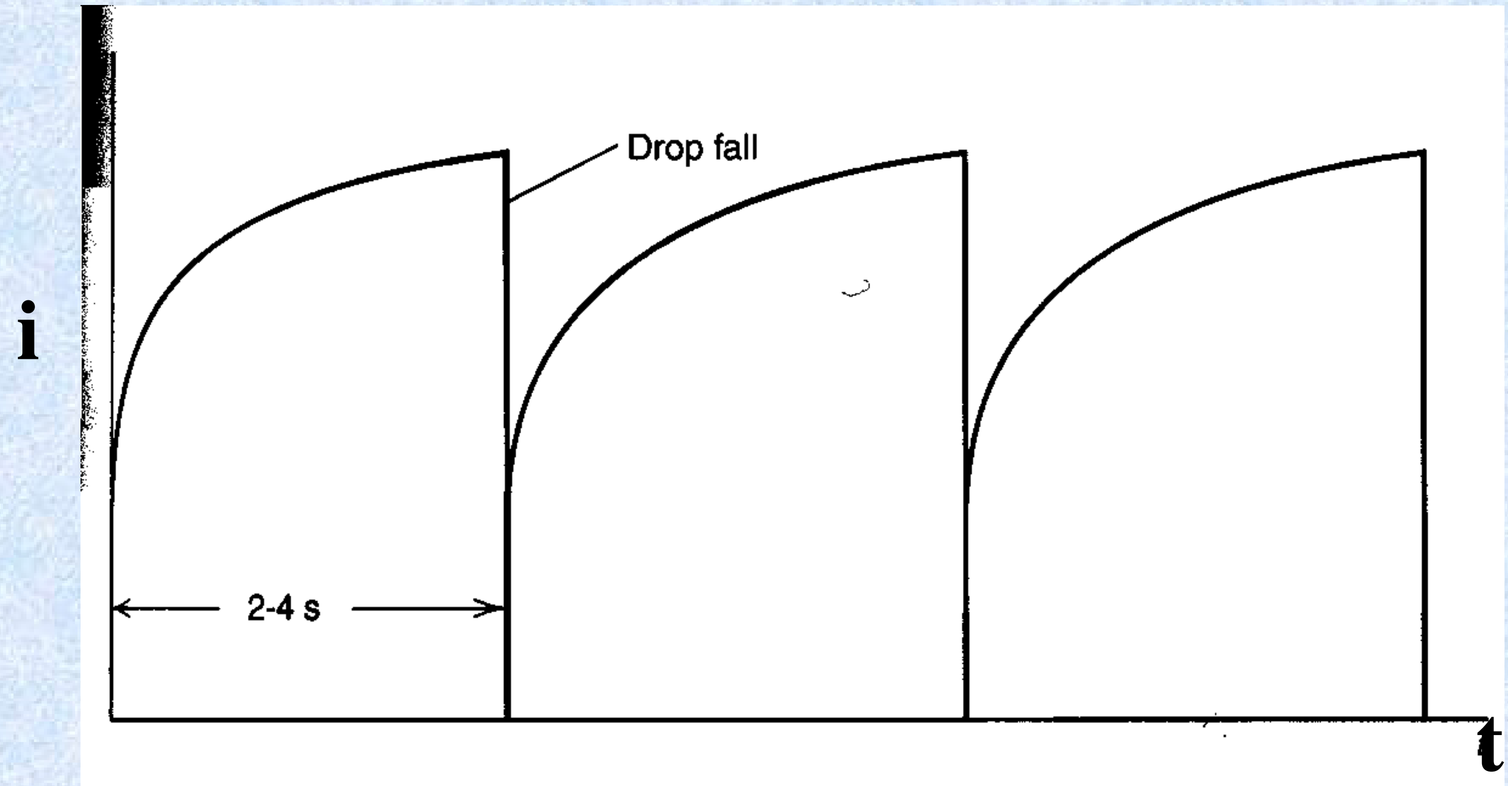
*Alejandro Baeza*


(galvanostático).
TÉCNICAS ELECTROQUÍMICAS
E = f (t)
i = f (t)
POTENCIAL
pulso
INTENSIDAD DE CORRIENTE
POTENCIOSTÁTICAS
GALVANOSTÁTICAS
POTENCIAL
barrido
INTENSIDAD DE CORRIENTE
POTENCIODINÁMICAS
GALVANDINÁMICAS 51
EGM
POLAROGRAFIA

## IV.4 Programa de perturbación y Patrón de respuesta para cada técnica

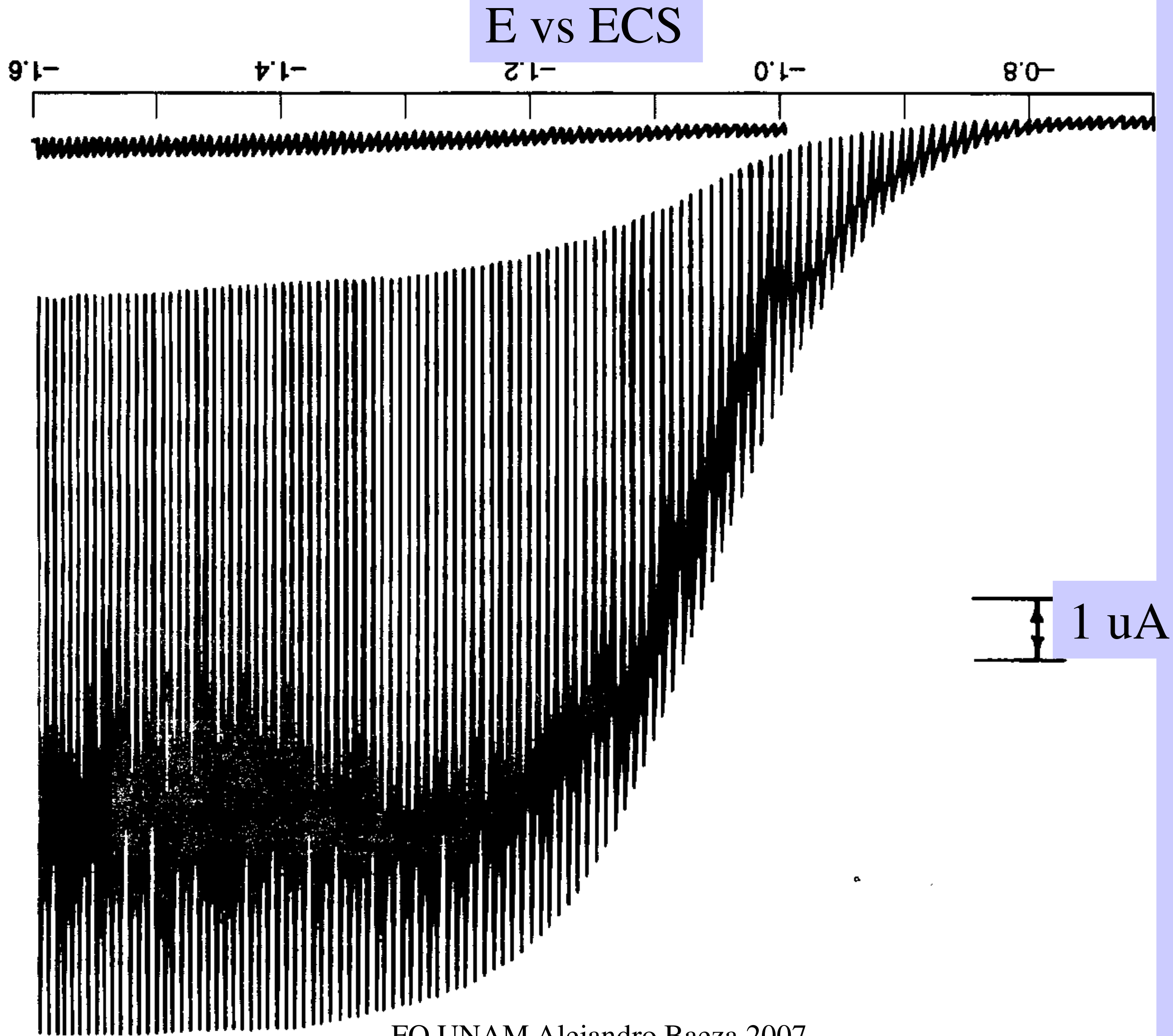
ALEJANDRO BAEZA

| Técnica | Programa de Perturbación | Respuesta |
|---|---|---|
| Cronoamperometría |   |   |
| Cronopotenciometría |   |  |
| Polarografía DC |   |   |
| Polarografía con barrido de corriente |   |  |
| Polarografía diferencial de pulsos. |   |   |




$$i_d = 708 n D_O^{1/2} C_O^* m^{2/3} t^{1/6}$$

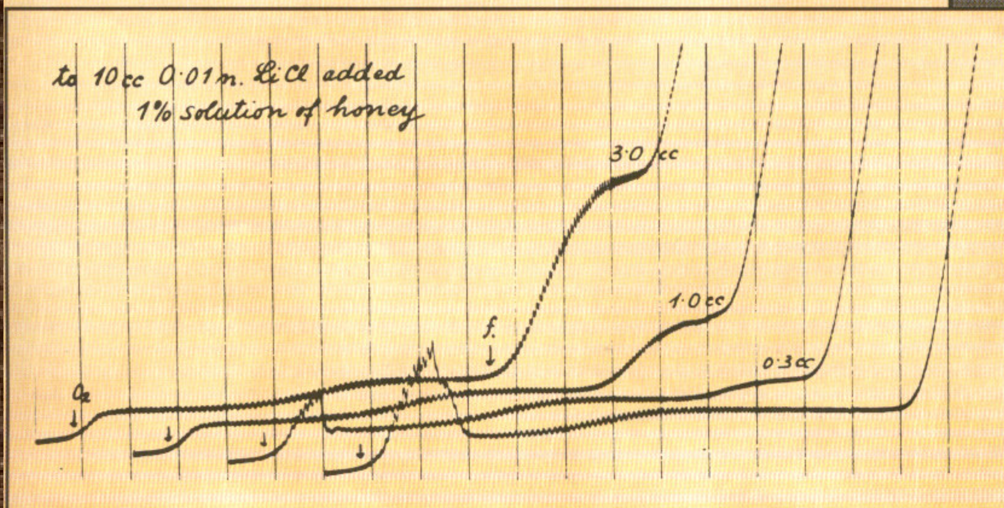
$$(i_d)_{max} = 708 n D_O^{1/2} C_O^* m^{2/3} t_{max}^{1/6}$$


E vs ECS
-1.6
-1.4
-1.2
-1.0
-0.8
1 uA

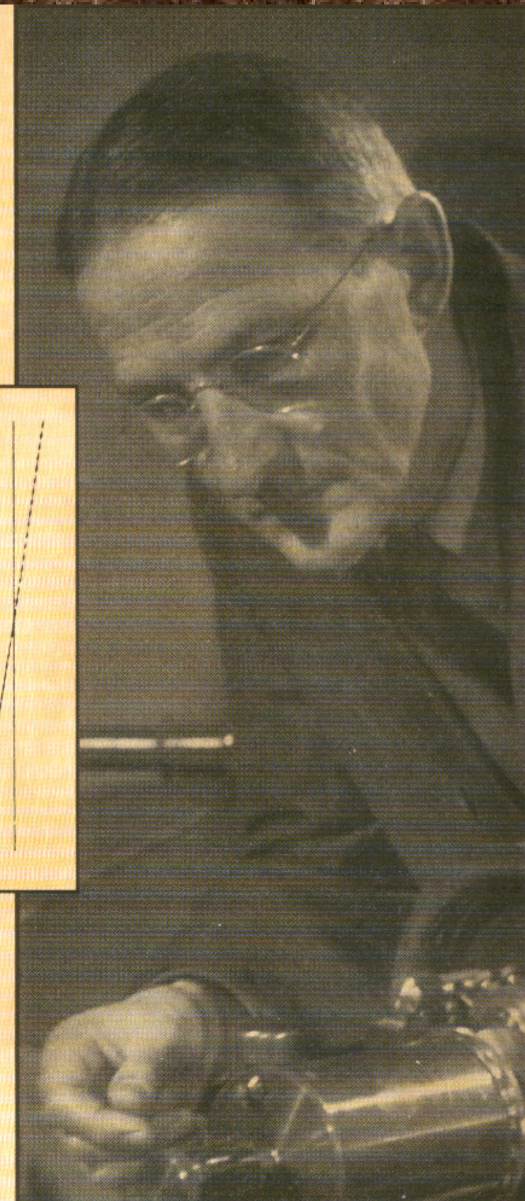
El profesor Jaroslav Heyrovský (1890-1967) y su polarógrafo, que describió por primera vez en 1922. El resultado lo registró en una película fotográfica.

By the early twentieth century, the concept of electroanalytical chemistry emerged as electrocapillary measurements were conducted with dropping mercury electrodes. The advent of polarography, as pioneered by Jaroslav Heyrovský, initiated rapid development of electroanalysis, culminating in powerful new techniques such as Osteryoung Square Wave Voltammetry.

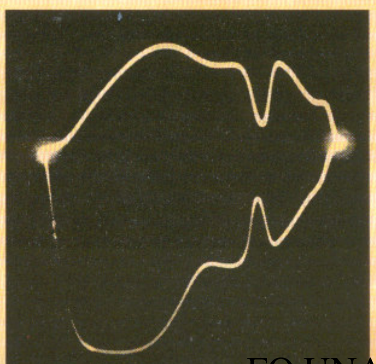
Although this calendar is by no means a comprehensive history, it does include some of the most influential members in the fraternity of electrochemists. Most of them did not consider themselves to be electrochemists, or even chemists. Physicians, engineers, natural philosophers and physicists predominate. As we move towards a new millenium, the uses of electrochemistry continue to flourish. Microelectrodes probe single cells, and fuel cells orbit the earth. We hope this calendar pays adequate homage to those scientists, from Galvani to Heyrovský, whose insights set us on the paths we follow to this day.




These original current-voltage curves depicting the reduction of fructose were monitored by a photographically-recording polarograph. The handwriting is Heyrovský's.

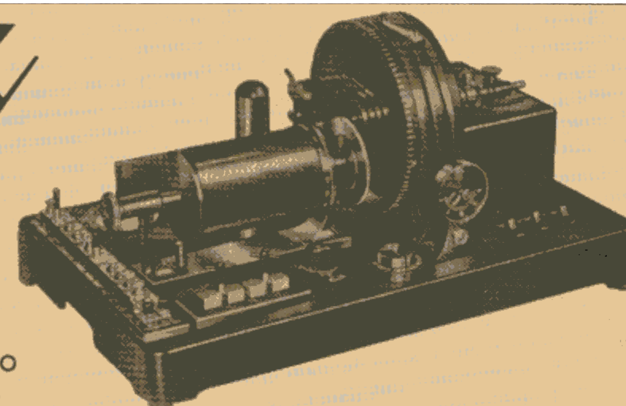


Jaroslav Heyrovský



Oscillographic polarography of riboflavin in 2 M $H_2SO_4$.

# HEYROVSKÝ



Nobel laureate Jaroslav Heyrovský (1890-1967) was born in Prague, the son of a law professor at Charles University. After a classical education in Prague, he advanced to University College (London) where he eventually worked as a student of F.G. Donnan in electrochemical research. At Donnan's suggestion, he began studies of liquid metal electrodes (aluminum amalgams) which were continuously renewed by delivery from glass capillaries. World War I interrupted his research in England and he was called to serve in the Austro-Hungarian army as a dispensing chemist. Nonetheless, he continued his experiments in the hospital pharmacy and was able to prepare a Ph.D. dissertation while still a soldier.

During his thesis defense at Prague University (1918), he met Prof. Kucera, who invited Heyrovský to join his research group to study the dropping mercury electrode (DME) for electrocapillary measurements. This was tedious work. A voltage was applied to a DME and a reference electrode was immersed in a test solution. After 50 drops of mercury were collected, they were dried and weighed. The applied voltage was varied and the experiment repeated. Measured weight was plotted vs. applied voltage to obtain the curve. Heyrovský continued this work in his own laboratory and eliminated the weighing step by monitoring drop-time. In 1921, he had the idea of measuring the current flowing through the cell instead of just studying drop-time. Using an amperometer, he made his first experiment on New Year's Day, 1922. It didn't work. Heyrovský was undaunted and borrowed a sensitive galvanometer to measure currents flowing from an electrolytic cell with a potentiometer as the voltage source.

On February 10, 1922, the "polarograph" was born as Heyrovský recorded the current-voltage curve for a solution of 1 mol $dm^{-3}$ NaOH. Heyrovský correctly interpreted the current increase between -1.9 and -2.0 V as being due to deposition of $Na^{+}$ ions, forming an amalgam. From this beginning, the measurement of polarographic current was extended to fundamental and theoretical studies of electrode processes, accompanying chemical reactions and analysis. Heyrovský was possibly the most powerful influence on the development of electroanalytical science in the twentieth century.

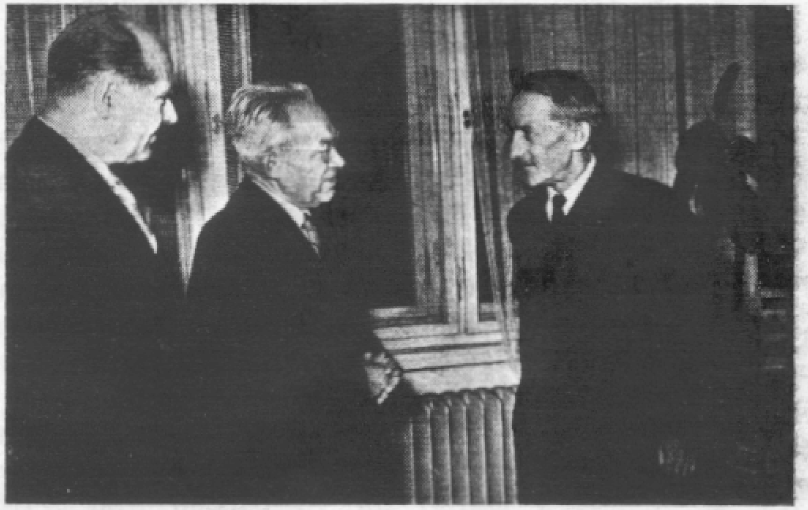


Figure 1. Professor Brdicka (far left) and Professor Laufburger, vice president of the Czechoslovak Academy of Science, congratulating Professor Heyrovsky on the occasion of the announcement of the Nobel Prize.

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Figure 2. Dr. Pribil, Dr. Kolthoff, and Dr. Heyrovsky (from left to right) in front of the old building of the Department of Physical Chemistry of Charles University in Prague, where polarography was born.

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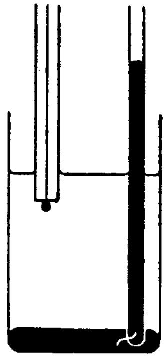
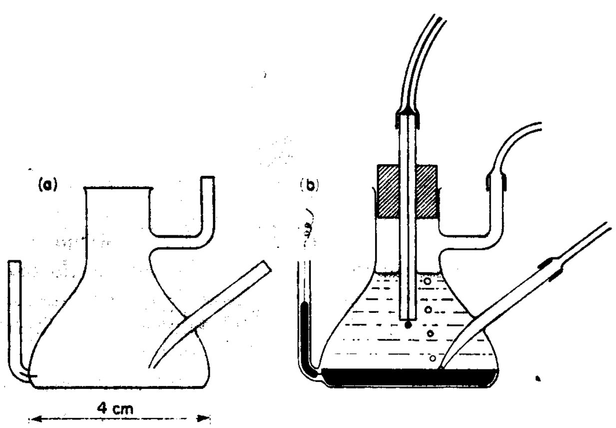
# Jaroslav Heyrovsky: Nobel Laureate

Figure 5. Sir C. Raman (Indian Nobel Prize winner) with Professor Heyrovsky in the garden of the Polarographic Institute, Prague.





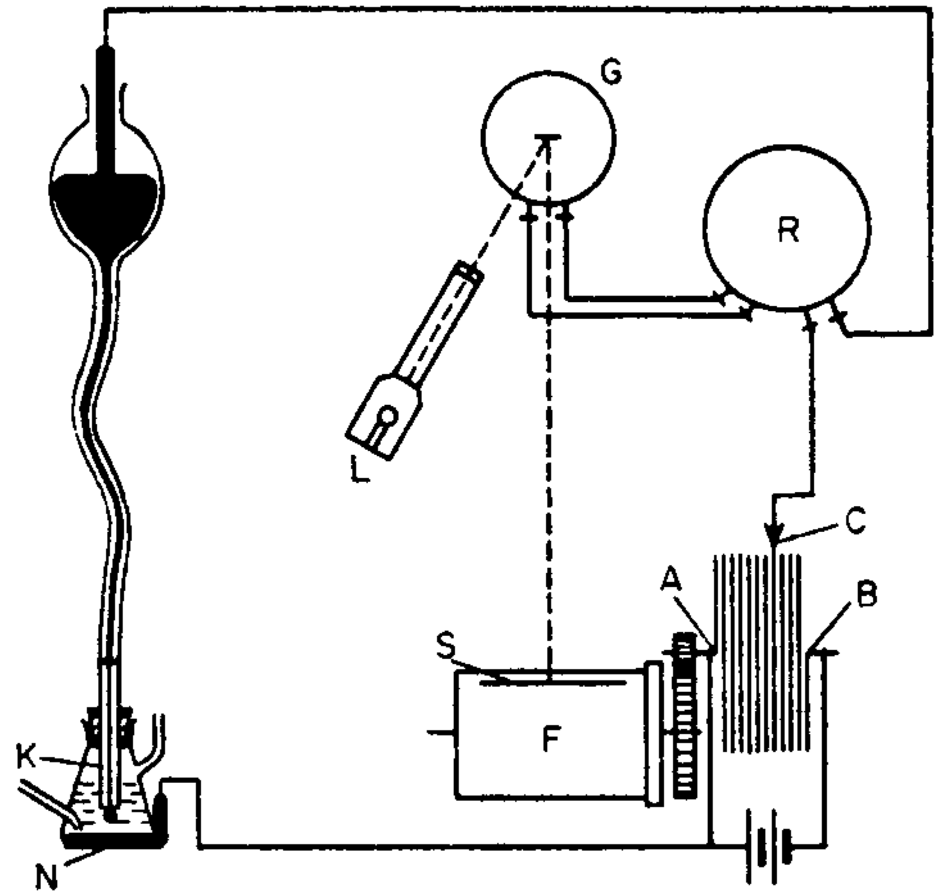




**Fig. 19.** Scheme of polarograph. (A)–(B) Potentiometric wire; (C) sliding contact; (F) photographic casette; (G) mirror galvanometer; (K) dropping electrode; (N) reference electrode; (R) galvanometer sensitivity reductor; (S) slit through which the beam enters the photographic casette.

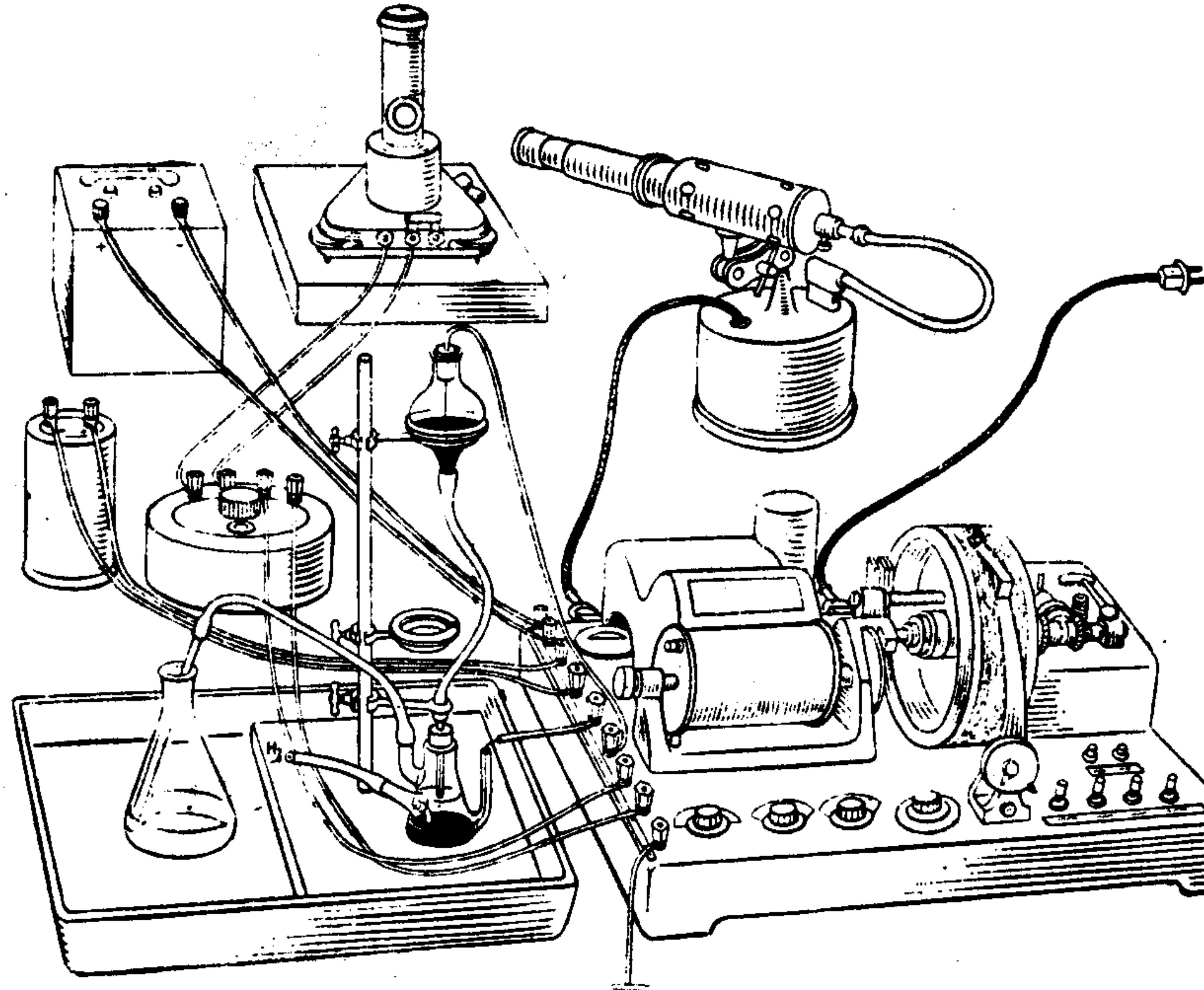
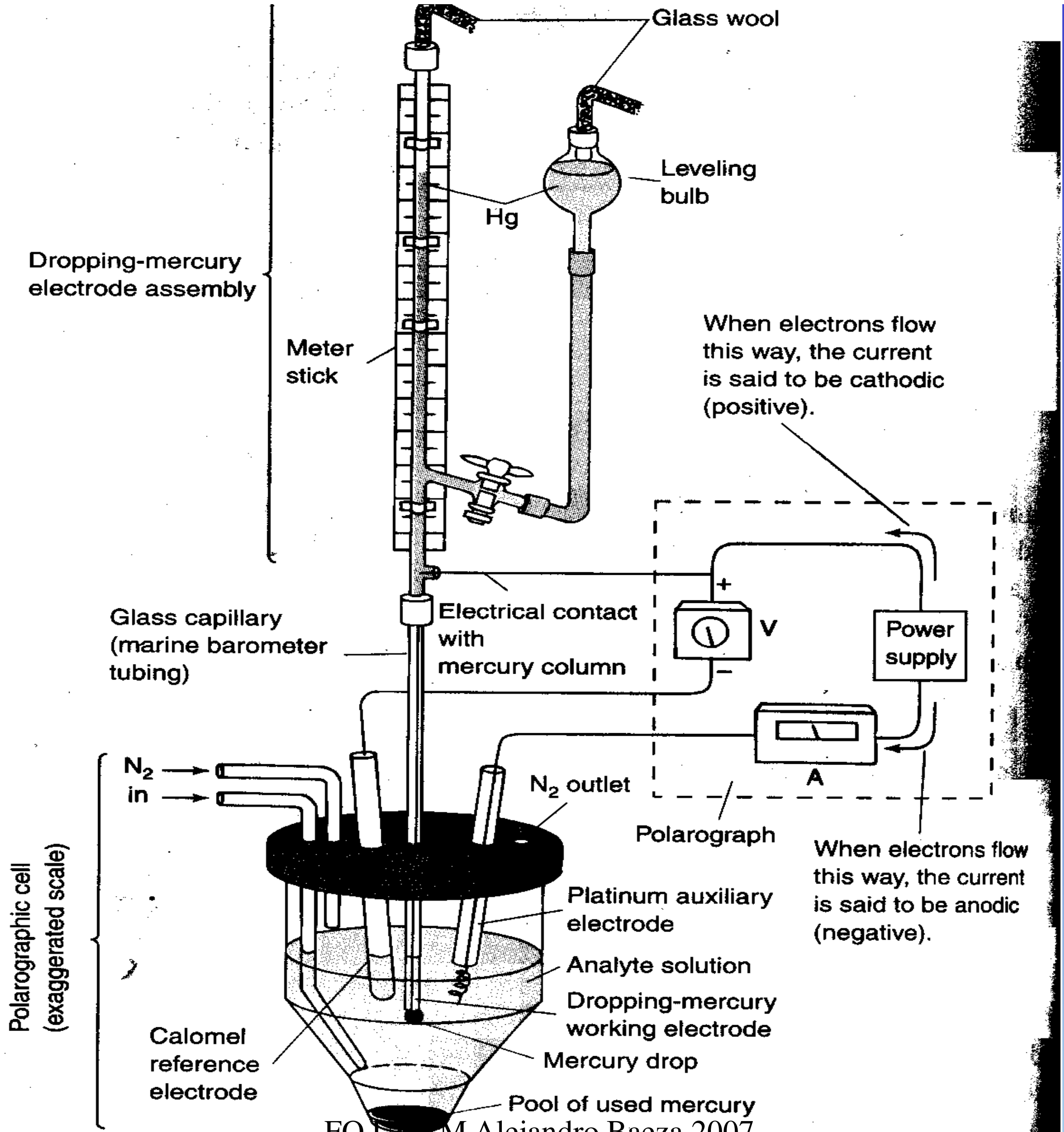
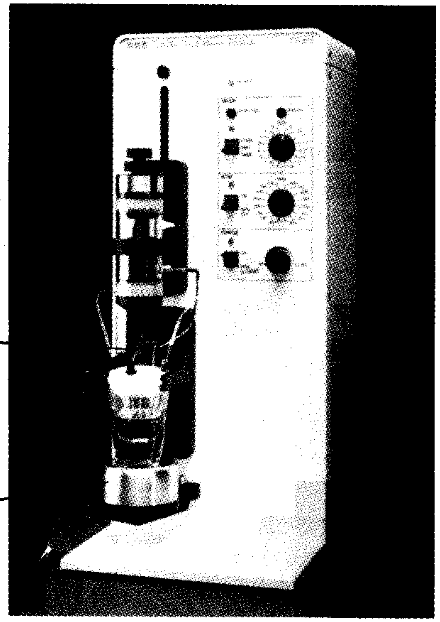
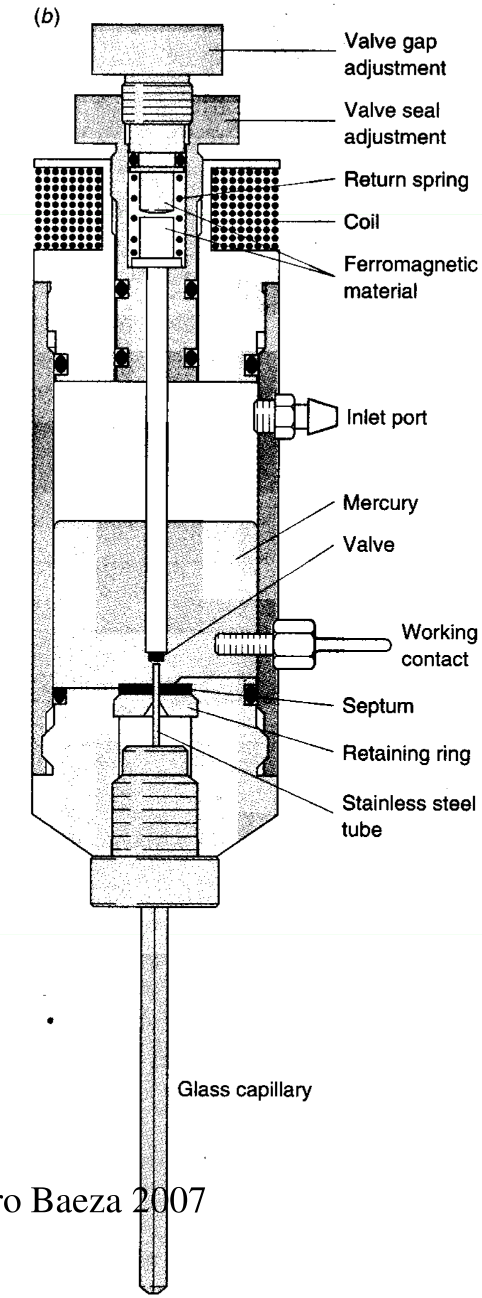


**Fig. 23. General view of the polarographic arrangement with the V 301 polarograph.**

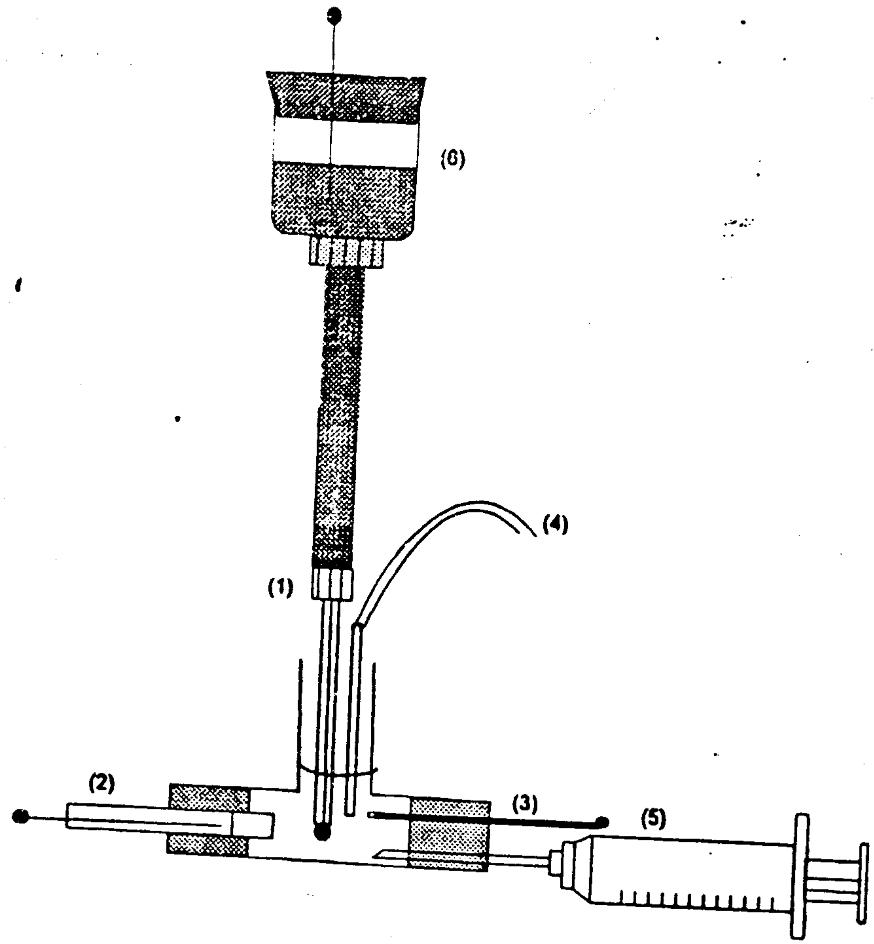

Glass wool
Leveling bulb
Hg
Dropping-mercury electrode assembly
Meter stick
When electrons flow this way, the current is said to be cathodic (positive).
Glass capillary (marine barometer tubing)
Electrical contact with mercury column
+
V
−
Power supply
A
$N_2$ in
$N_2$ outlet
Polarograph
When electrons flow this way, the current is said to be anodic (negative).
Polarographic cell (exaggerated scale)
Platinum auxiliary electrode
Analyte solution
Dropping-mercury working electrode
Mercury drop
Calomel reference electrode
Pool of used mercury



18-2 Shape (




-2 (*a*) Modern polarographic equipment
ercury electrode, sample cell, and controls. (The
an also be controlled entirely from software on
er unit that is not shown.) (*b*) Schematic of
ectrode. Mercury from the internal reservoir
lass capillary through the stainless steel tube.
valve is held in the closed position by the return
e top of the assembly. Electrical current
the coil at the top of the assembly to open the
precisely determined time to allow a mercury
desired size to form before the valve closes
r measuring current and voltage with the static,
op, the drop is dislodged by a mechanical drop
ot shown) and a new drop of exactly the same
ensed. Continuous electrical contact is made to
y column via the stainless steel tube even when
closed. [Courtesy Bioanalytical Systems, West
N.]

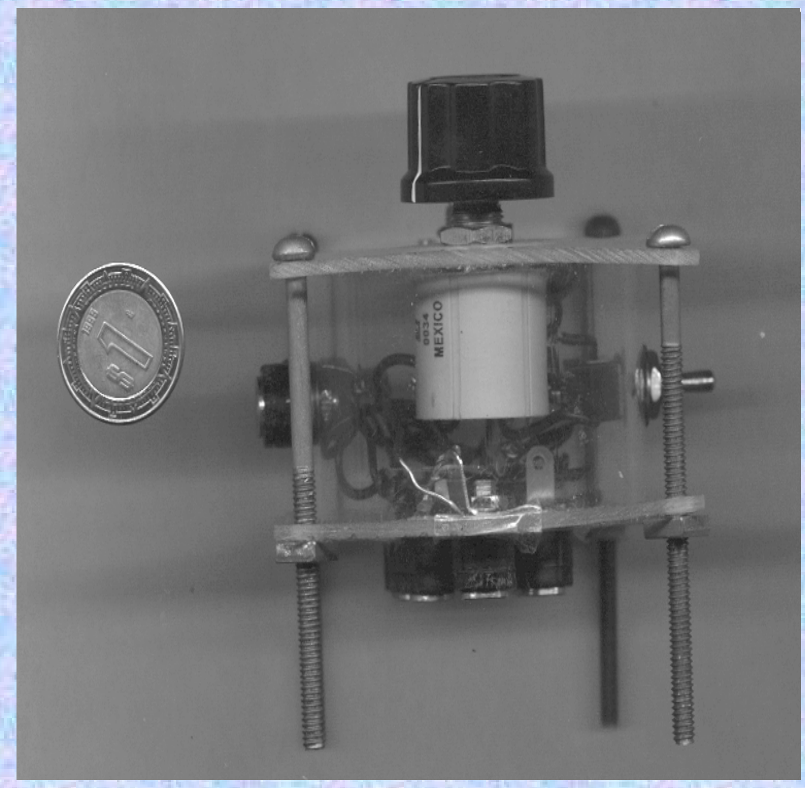


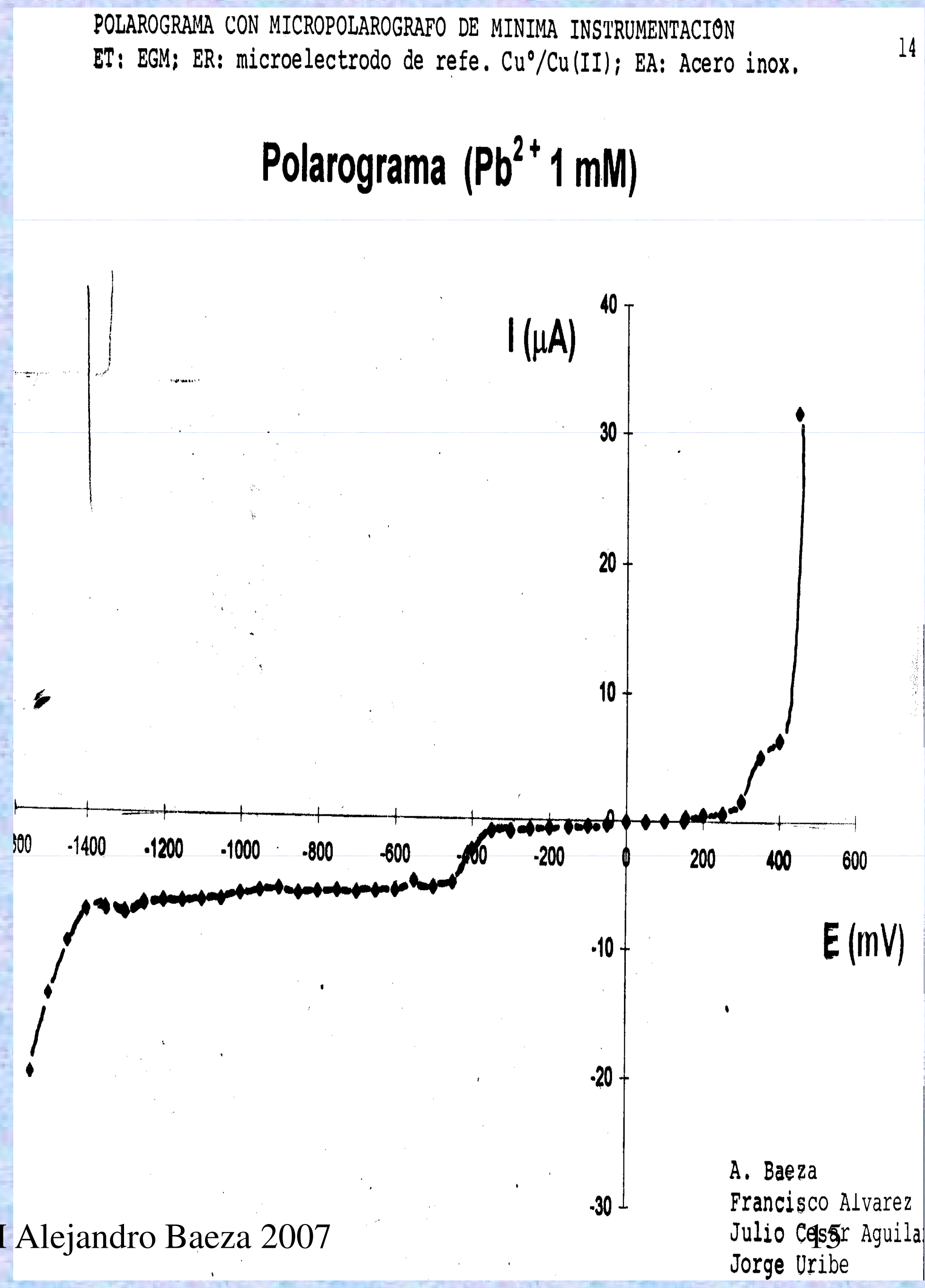

**F2**

Micropolarographic cell, V=500 µL. 1) DME; 2) Reference electrode Ag°|AgCl↓|KCl 0.1M||; 3) C° auxiliary electrode; 4) nitrogen inlet; 5) Hg° purge; 6) Hg° pool.

**POLAROGRAPHIC DETERMINATION OF Km´ AND Vmax OF GLUTATHIONE REDUCTASE**

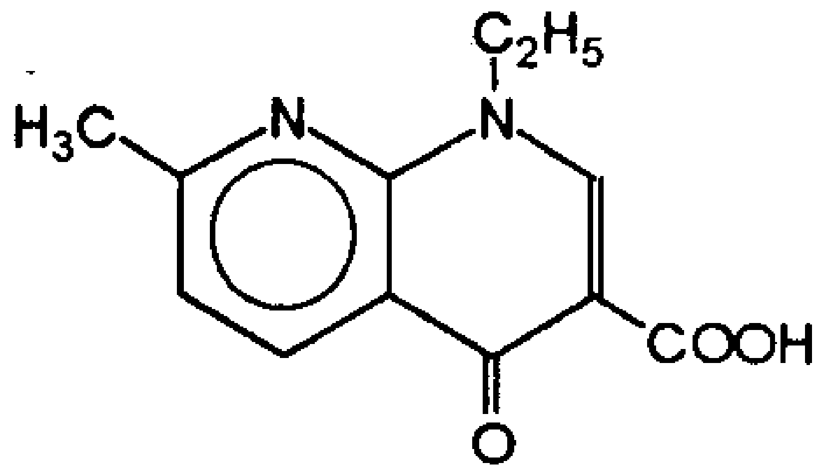
***Current Separations. 2003.***




POLAROGRAMA CON MICROPOLAROGRAFO DE MINIMA INSTRUMENTACIÓN
14
ET: EGM; ER: microelectrodo de refe. Cu°/Cu(II); EA: Acero inox.
Polarograma (Pb2+ 1 mM)
I (µA)
E (mV)
40
30
20
10
0
-10
-20
-30
-1400
-1200
-1000
-800
-600
-400
-200
0
200
400
600
A. Baeza
Francisco Alvarez
Julio César Aguilar
Jorge Uribe

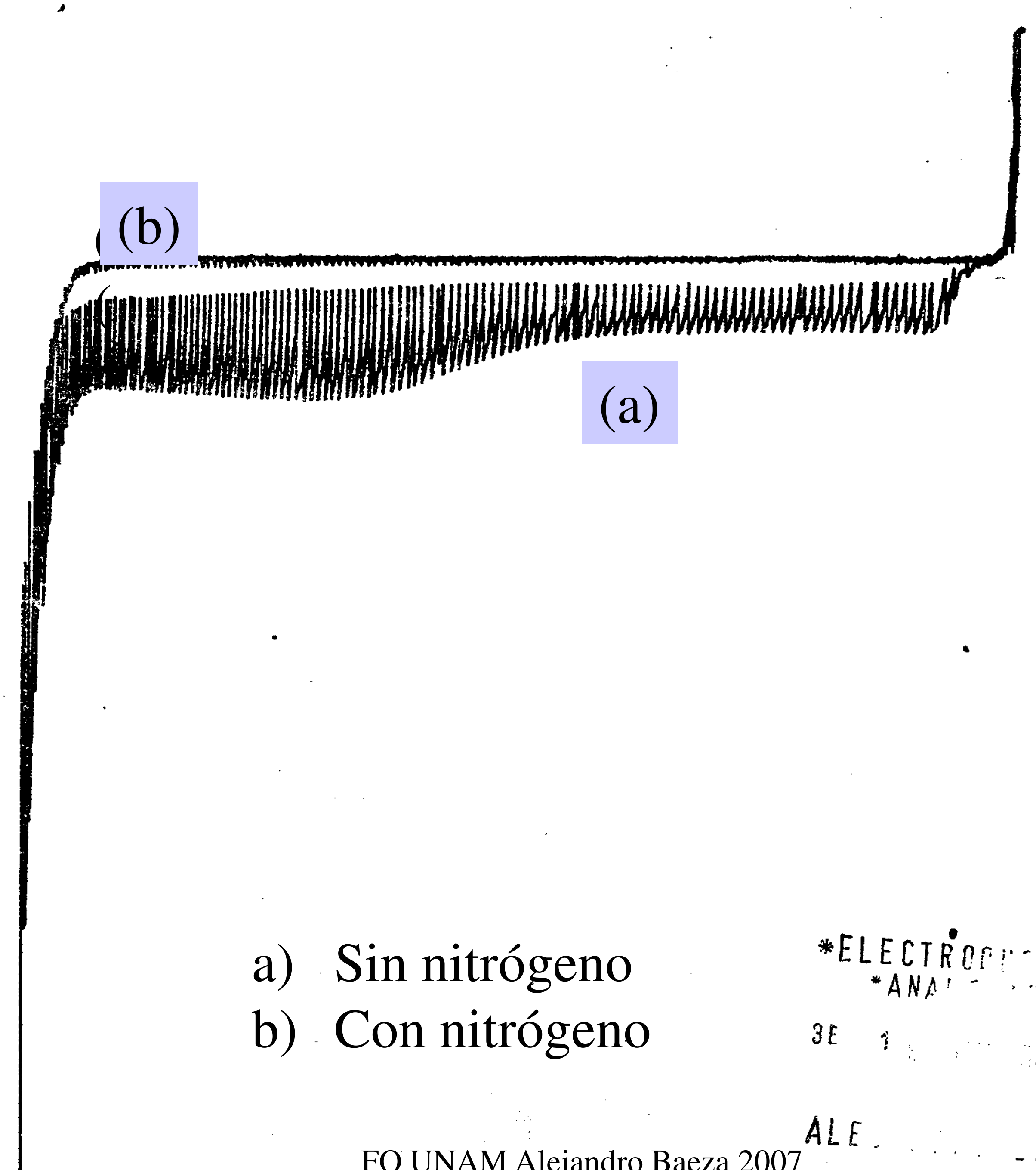
# *MIMP*

# NALIDIXICO, ACIDO

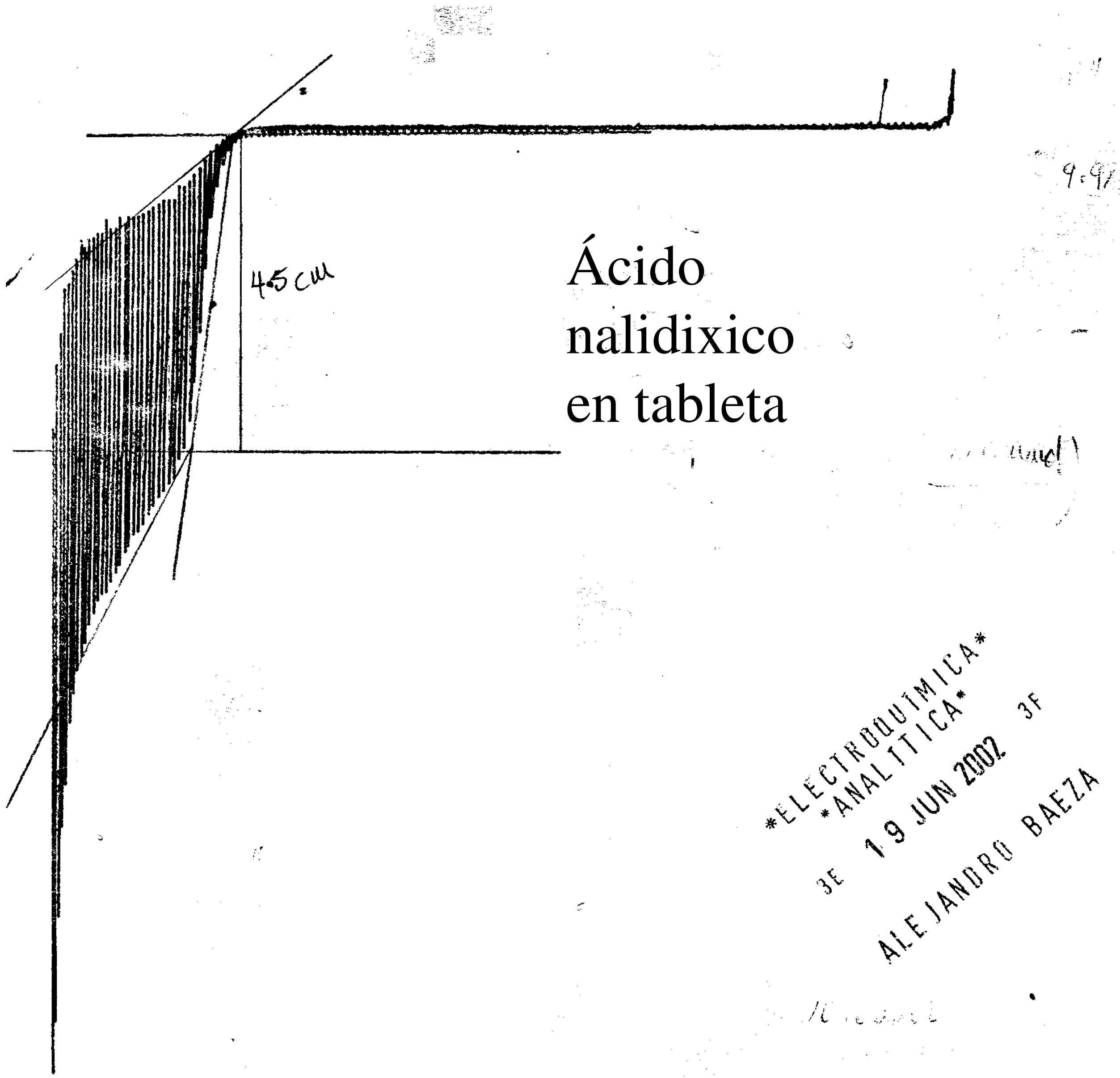



$C_{12}H_{12}N_2O_3$

MM 232.24

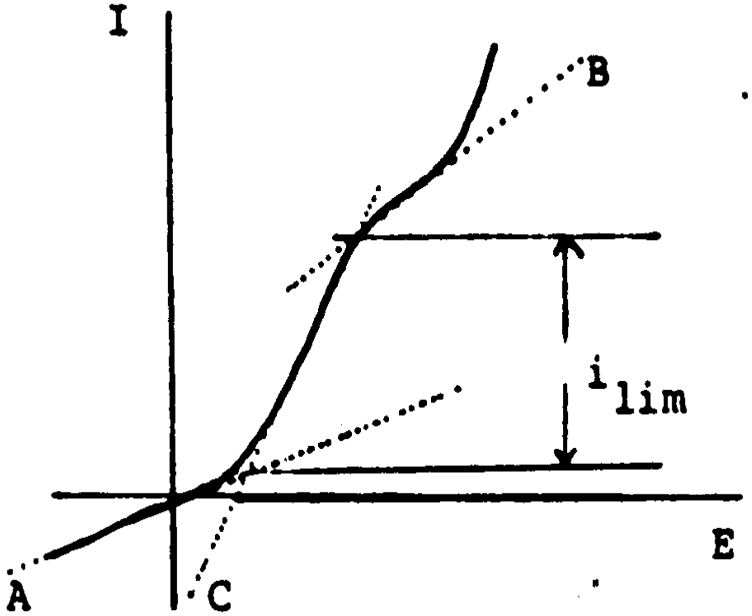


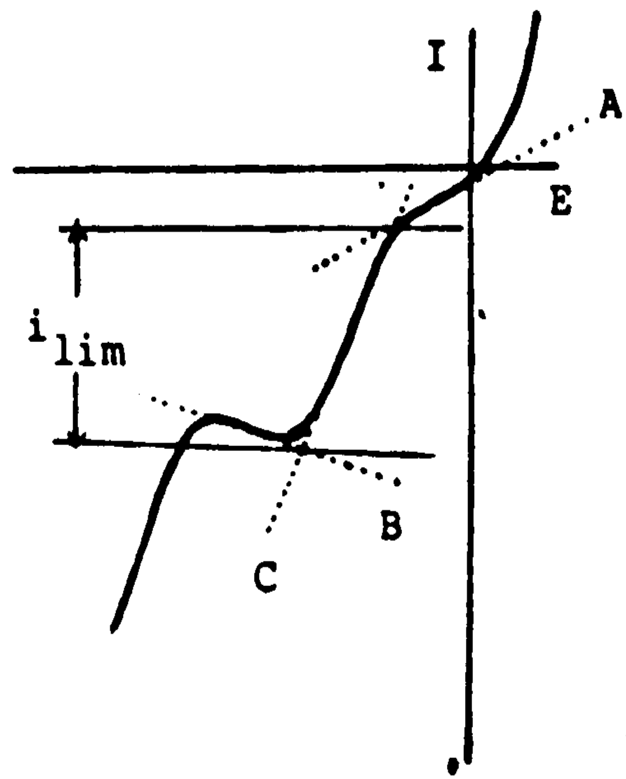

a) Sin nitrógeno
b) Con nitrógeno




Ácido nalidixico en tableta

Se muestran dos ejemplos de medición de la corriente límite:



*ELECTROQUIMICA*
*ANALITICA*

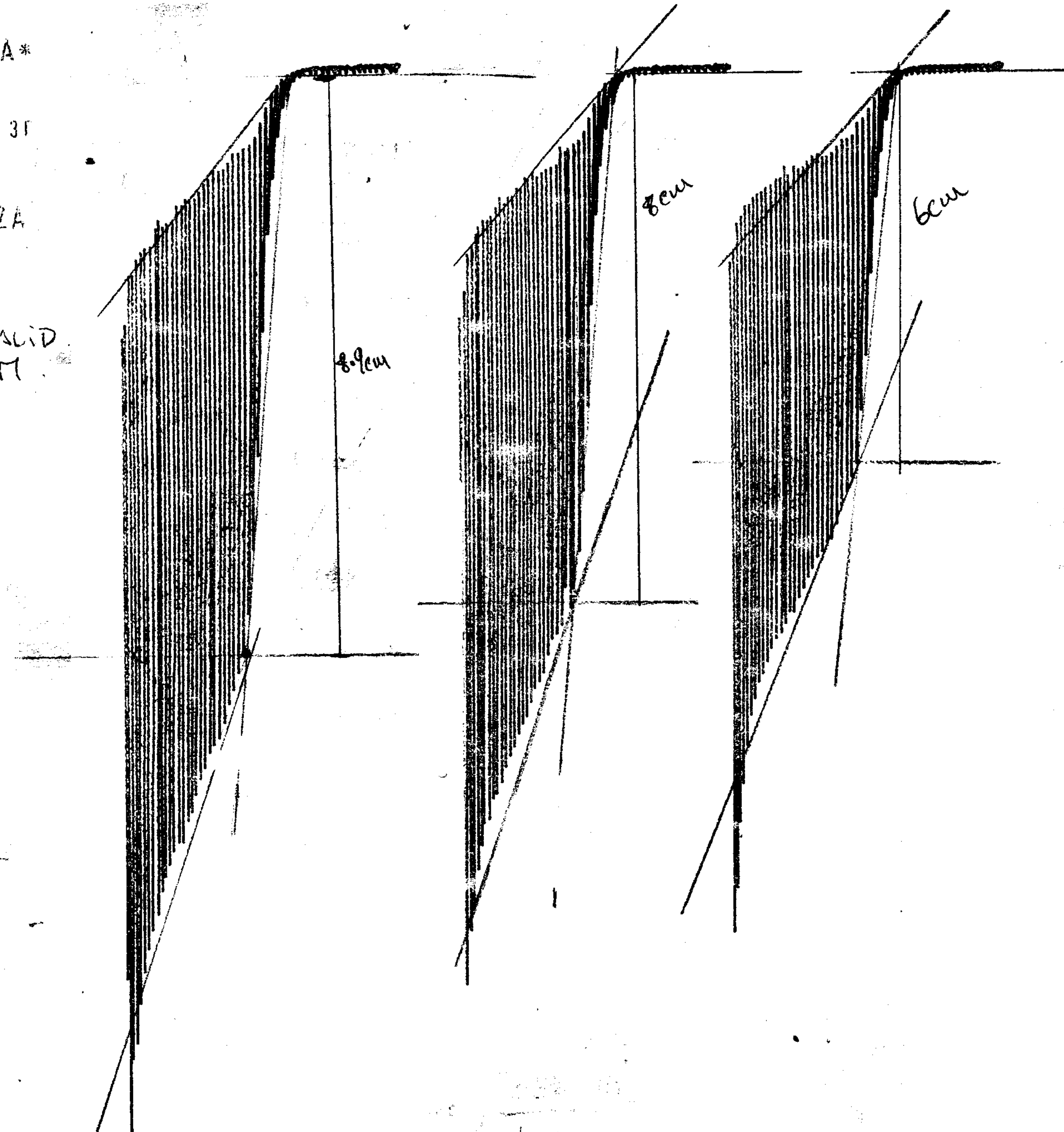
19 JUN 2002

ALEJANDRO BAEZA

Idem ②

+ 100 μL STD NaCl 0.1 M.

$E_i = -1.3$ V



Si $C_s$ se varía deliberadamente para obtener una serie de valores para $R$, el gráfico de $R$ en función de $C_s$ tendrá el aspecto ilustrado en la fig 3.13 (recuerda que $kC_x$ es una constante, aun cuando sea desconocida).

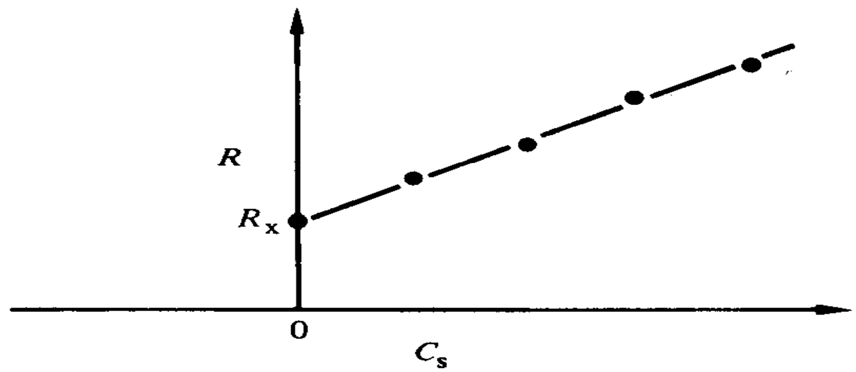



**Figura 3.13**

Para encontrar el valor de $C_x$ (el cual, después de todo, es el objeto de estas mediciones), solamente es menester extrapolar la recta hasta su intersección con el eje horizontal, en donde $R$ es cero (fig. 3.14).

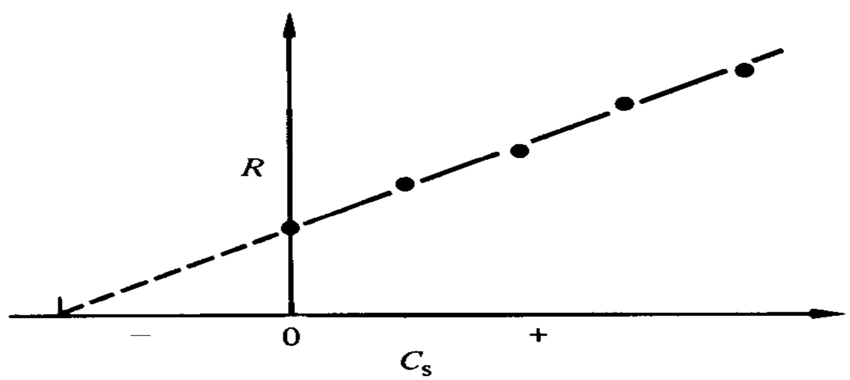
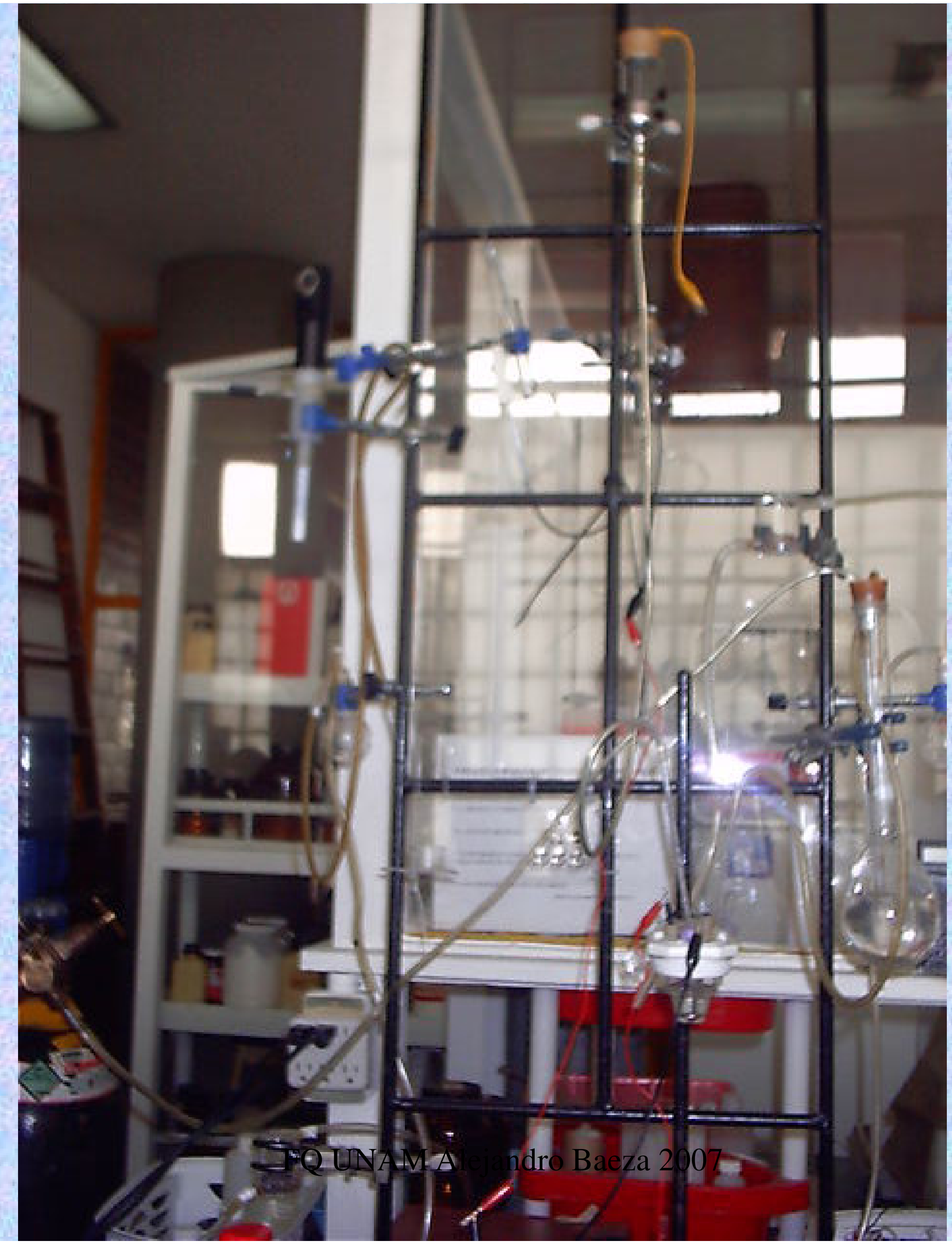
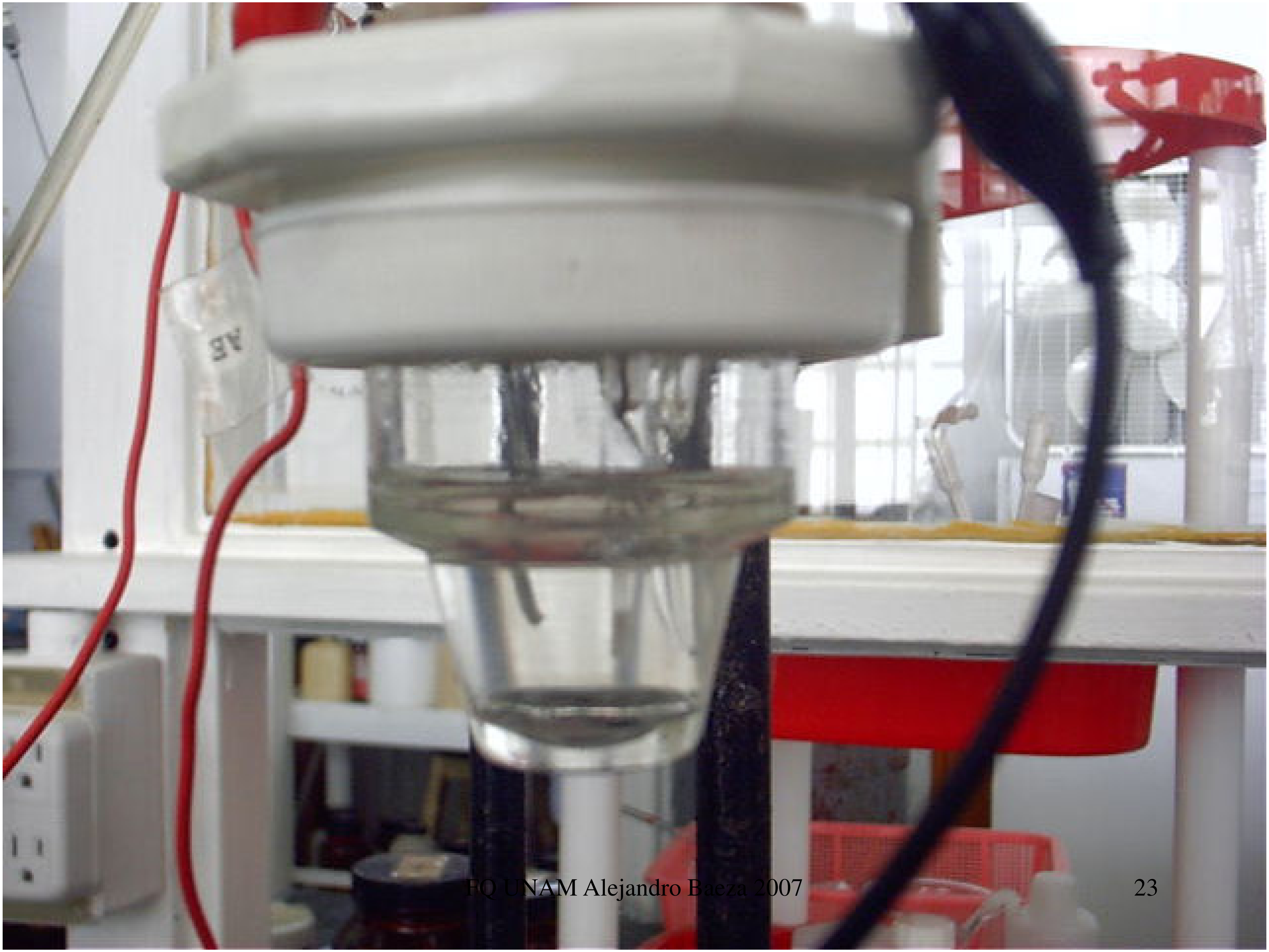
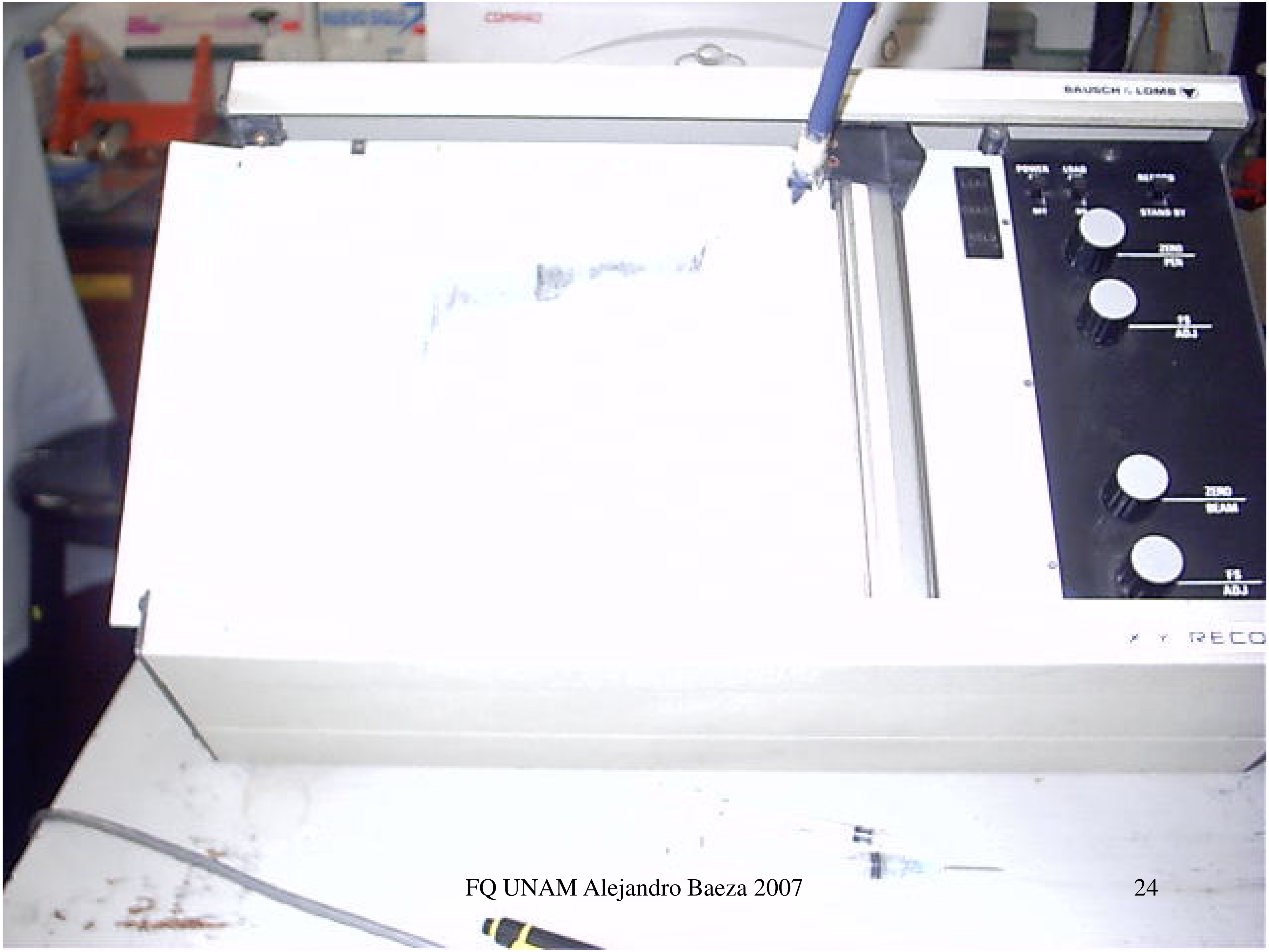



**Figura 3.14**






BAUSCH & LOMB
ZERO
PEN
FS
ADJ
ZERO
BEAM
FS
ADJ
X Y RECO