

COULOMETRIC TITRATION OF STRONG ACID IN PRECIPITATION1. PRINCIPLE

The method is based on the coulometric titration method by Liberti et al (1), in which the acid is titrated at constant current with hydroxyl ions liberated at a platinum electrode with a silver, silver bromide electrode serving as the counter electrode. The total reaction is:



The e.m.f. of a glass - calomel electrode pair is read at intervals and the results are used to construct a Gran's plot (2,3), which gives the endpoint by extrapolation of the straight portion of the curve.

The only necessary modification is the addition of a constant, known amount of acid to the samples before the titration to facilitate the titration of weakly acidic or alkaline samples without interference from carbon dioxide.

2. INSTRUMENTS AND EQUIPMENT

2.1. Expanded-scale pH-meter

Radiometer PHM 26 or an instrument with similar specifications.

2.2. Constant current source (2-10 mA adjustable)

A 4.5 V dry battery with an adjustable series resistance and a mA meter is sufficient, but "coulometers" are available commercially, e.g. from Metrohm (Metrohm A.G., Herisau).

2.3. Titration vessel, 50 ml

This should have a suitable lid with 5 holes to serve as support for the electrodes and the nitrogen inlet. Suitable titration assemblies are:

- Radiometer TTA3
- Metrohm EA 880-50 (T).

The latter can be supplied with a thermostat jacket on request. Treatment of the titration vessel with dimethyl-dichlorosilane is useful for easy rinsing and reduction of contamination.

The titration assembly with electrodes in use in the laboratory of the Norwegian Institute for Air Research is shown in Fig. 1.

2.4. Thermostat ($25^{\circ} \pm 1^{\circ}$)

2.5. Electrodes

Ordinary glass electrode 0-10 pH range and calomel reference, electrode for instance Radiometer G 202 C and K 101.

Platinum sheet electrode, 0.75 by 1.25 cm, made of bright platinum foil.

Silver wire. The silver, silver bromide electrode is made from 99,9 % pure, 1.0 mm dia. wire, about 30 cm long and coiled to a suitable dimension.

2.6. Micropipette

0 - 2.5 ml for the addition of known amounts of 0.01 N H₂SO₄ to the samples before the titration.

2.7. Distillation and deionization equipment

The water for rinsing, preparation of solutions and standards etc should be distilled in an all-glass still, deionized by ion exchange and finally filtered through a membrane filter. Store in polyethylene containers. The specific conductances of the product should be less than $1 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$.

2.8. Solutions

2.0 M KBr solution
0.01 N H₂SO₄

3 PROCEDURE

Pipet 50 ml of the solution into the titration vessel. Add 500 μl KBr solution (2.0 M) and exactly 500 μl 0.01 N H₂SO₄. If the pH of the sample is above 5.6 it may be necessary to add more than one 500 μl portion of 0.01 N sulphuric acid.

Start nitrogen purging and adjust flow to give continuous agitation of the solution. The bubbles should not disturb the solution between the sensing or the working electrodes.

Wait until pH reading is constant. Switch pH meter to read millivolts (range 0 - 240 mV with glass electrode positive) and start the electrolysis current.

Read the glass electrode potential vs the calomel electrode every 20 seconds and continue until the potential changes sign (at pH 8). Stop the electrolysis.

Plot Gran's function $\Psi = 10^{EF/RT} \ln 10$

(F = Faradays constant, R = The universal gas constant, T = absolute temperature).

($\Psi = 10^{-E(\text{mV})/59.15}$, at 25°C)

against electrolysis time (in seconds). The plot intercepts the abscissa at the equivalence point, t_e .

The concentration of strong acid in the sample is calculated from the formula:

$$C_{H^+} = \frac{i \cdot t_e}{F \cdot V_o} \div \frac{N_{H_2SO_4} \cdot V_{H_2SO_4}}{V_o}$$

or

$$= \frac{i \cdot t_e \cdot 1000}{96\ 500 \cdot 50} \div 1 \cdot 10^{\div 4} \text{ moles/l}$$

where

- i = electrolysis current in ampères
- t_e = electrolysis time at equivalence point (seconds)
- F = Faradays constant (coulombs/mol)
- V_o = Initial sample volume (liters)
- $N_{H_2SO_4}$ = Normality of added sulphuric acid
- $V_{H_2SO_4}$ = Volume of added sulphuric acid (liters)

4 COMMENTS

The procedure outlined above is applicable to samples with concentrations of strong acids in the range 10^{-5} - 10^{-3} M. Higher acidities are not expected. The lower concentration limit is close to the background values expected and is also very close to the lowest concentration which can be said to be harmful from a biological point of view. The standard deviation of the titration values is around 2-5 μ equiv./l ($0.1 - 0.2 \cdot 10^{-5}$ M) for samples in the range $1 \cdot 10^{-5}$ - $1 \cdot 10^{-4}$ M and 1-2% relative for samples with higher acidities.

Tests with sampling containers and storage of samples show that polyethylene and borosilicate glass can be used. The glass ware must be treated with hot dilute acid and thoroughly soaked in distilled water before being put to use.

12 hours with 10% hydrochloric acid at 90°C followed by 24 hours soaking in distilled water is considered adequate. Otherwise, alkalis from the glass will diffuse into the samples. These precautions are similar to the precautions taken with glass ware to be used for sodium flame photometric determinations in the ppm range. When rainwater samples are stored in polyethylene containers, the concentration of acid seems to increase slightly during storage.

5 REFERENCES

1. Liberti, A: Possanzini, M: Vicedomini, M:
The Determination of the Non-Volatile Acidity of
Rain Water by a Coulometric Procedure.
Analyst, 97, 352-356 (1972).
2. Gran, G, Analyst, 77, 661-671 (1952).
3. Rossotti, F.J.C, and Rossotti, H, J. Chem. Educ. 42, 375.
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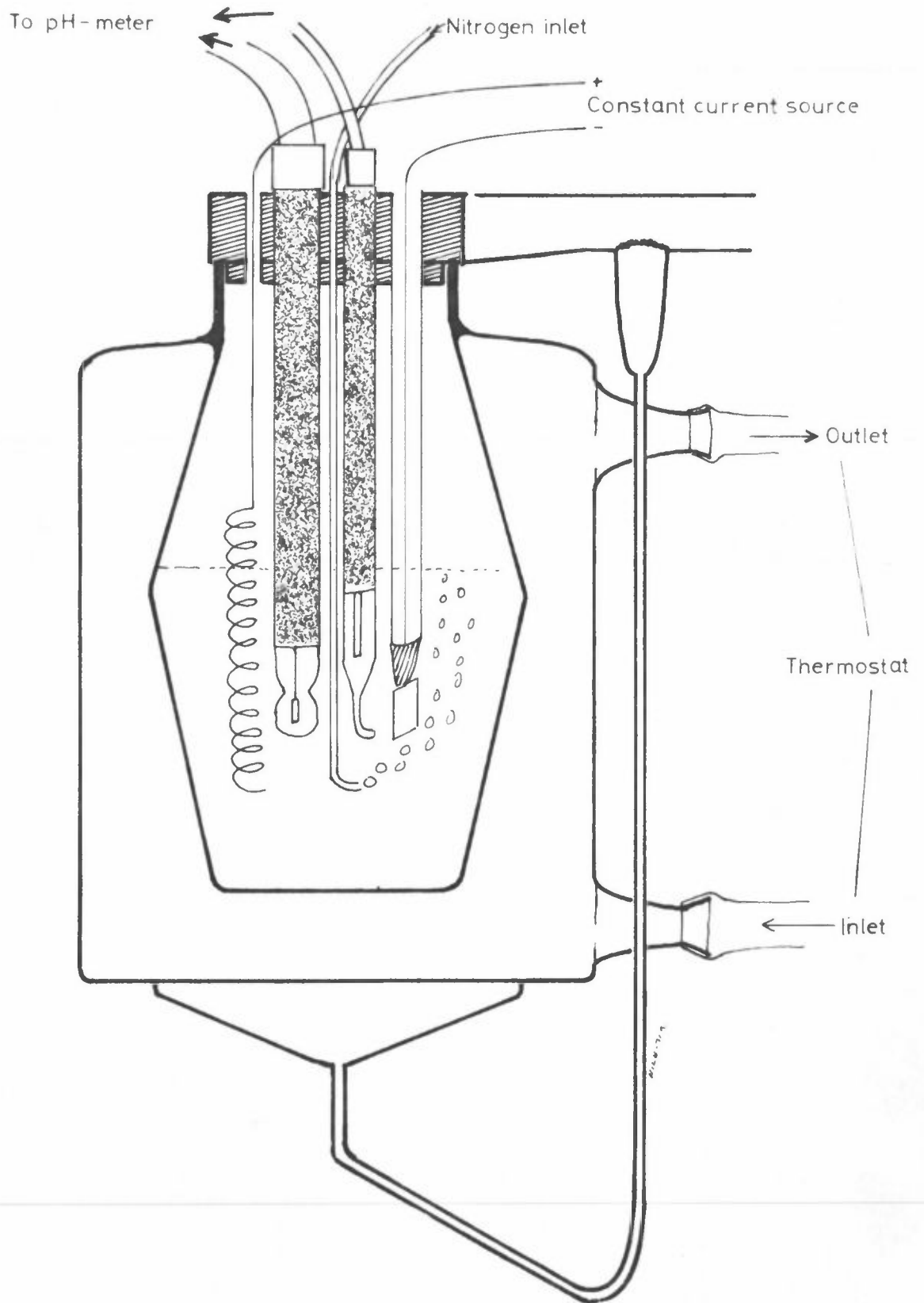


Fig.1. Titration vessel and electrode assembly

TABLE 1 - Gran's function $\Psi = 10 \frac{E}{59.15}$ calculated for
(0 - 160 mV)

E mV	Ψ	E mV	Ψ	E mV	Ψ	E mV	Ψ
1	1.04	41	4.93	81	23.4	121	111
2	1.08	42	5.13	82	24.4	122	115
3	1.14	43	5.33	83	25.3	123	120
4	1.17	44	5.55	84	26.3	124	125
5	1.22	45	5.77	85	27.4	125	130
6	1.26	46	5.98	86	28.4	126	135
7	1.31	47	6.22	87	29.6	127	140
8	1.36	48	6.47	88	30.7	128	146
9	1.42	49	6.75	89	32.0	129	152
10	1.48	50	7.00	90	33.3	130	158
11	1.54	51	7.28	91	34.6	131	164
12	1.60	52	7.57	92	36.0	132	171
13	1.66	53	7.87	93	37.4	133	177
14	1.73	54	8.19	94	38.8	134	185
15	1.80	55	8.51	95	40.4	135	192
16	1.90	56	8.85	96	42.0	136	199
17	1.94	57	9.20	97	43.6	137	207
18	2.02	58	9.57	98	45.3	138	216
19	2.10	59	9.94	99	47.2	139	224
20	2.18	60	10.3	100	49.1	140	233
21	2.26	61	10.7	101	51.0	141	242
22	2.36	62	11.1	102	53.1	142	252
23	2.45	63	11.6	103	55.2	143	262
24	2.54	64	12.1	104	57.4	144	272
25	2.65	65	12.5	105	59.7	145	283
26	2.75	66	13.0	106	61.9	146	294
27	2.86	67	13.5	107	64.4	147	306
28	2.97	68	14.1	108	67.0	148	318
29	3.09	69	14.6	109	69.7	149	331
30	3.21	70	15.2	110	72.4	150	344
31	3.34	71	15.8	111	75.3	151	351
32	3.48	72	16.5	112	78.3	152	371
33	3.61	73	17.1	113	81.5	153	386
34	3.75	74	17.8	114	84.7	154	402
35	3.90	75	18.5	115	88.1	155	418
36	4.06	76	19.3	116	91.6	156	434
37	4.23	77	20.0	117	95.1	157	452
38	4.39	78	20.8	118	98.9	158	470
39	4.56	79	21.7	119	103	159	489
40	4.74	80	22.5	120	106	160	507

APPENDIX

AUTOMATIC PLOTTING OF GRAN'S FUNCTION BY
MEANS OF AN ELECTRONIC ANALOG ELEMENT

1 PRINCIPLE

The output signal from the pH-meter is biased, amplified and modified by electronic circuitry to give a resulting signal which is proportional to the hydrogen ion concentration in the solution and which can be recorded on an ordinary potentiometric strip-chart recorder with constant paper speed.

Since the volume of the solution is not altered during the titration, and the hydroxyl is supplied at a constant rate, this procedure gives Gran's plots directly.

2 CONSTRUCTION

A block diagram showing the complete instrumental lay-out is shown in Figure A1 and the construction of the electronic unit is shown in Figure A2. The recorder output from the pH-meter is used as input signal to the unit. The 0.1 mV/1 mV output of the Radiometer PHM 26 was selected. The pre-amplifier (μ A 709) has a gain of 169, which gives an output voltage of 1 V for a change in the hydrogen ion activity of one decade.

The logarithmic amplifier gives an output signal of 10 mV to 10 V for an input signal of -1 to 2 volts.

The μA -709 preamplifier is biased with reference to the ground of the PHM 26 recorder output. The bias voltage is stabilized with a Zener diode, and can be varied to ensure that the signal is within the working range of the amplifier.

The amplification of the μA 709 preamplifier is adjusted by variation of the input resistance.

3 CALIBRATION

Adjust the bias voltage to bring the output of the amplifier within the working range using buffer solutions of pH 4-5, then adjust the gain of the μA 709 to 169 using digital volt meters at the input and output of the μA 709. This gain should be within $\pm 5\%$. (A deviation of about 25% from this figure is necessary to introduce a noticeable titration error or deviation from linearity of the Gran's plots obtained.)

The procedure may have to be repeated.

3.1 Operation

Pipet 50 ml of the sample into the titration vessel. Add exactly 1 ml of a solution 1 M KBr in 0.005 N sulphuric acid. Measure pH. If the pH of the solution is still above 4.00, successive amounts of 0.005 N sulphuric acid are added until the pH of the solution is less than 4.0.

Switch the pH-meter to the mV-position, recorder on and start stirring or bubbling nitrogen to agitate the solution.

Select the electrolysis current (3-5 mA) and start the titration. This will result in a "jump" on the recorder trace, because the electrode potential is affected by the potential between the working electrodes. By proper positioning of the electrodes, this effect should be minimized. Continue the electrolysis until the recorder signal is zero. Stop the electrolysis and the recorder. Note the sample identification, electrolysis current, and the amount of acid added on the recorder sheet. The concentration of strong acid is calculated from the formula:

$$C_{H^+} = 10^6 \cdot \frac{I \cdot l \cdot 1000}{v \cdot F \cdot V} - C_{H^+} \text{ (added)}$$

- I: electrolysis current (amperes)
- v: paper chart speed (cm/min) → mm/sec
- l: length of paper from start of titration current to the equivalence point, in mm
- F: Faradays number: 96 500
- C_{H^+} : (added) will normally be 100 (μeq/litre)
- V: sample volumemillimeter (Normally 50)

A titration graph for an actual precipitation sample is given in Figure A4.

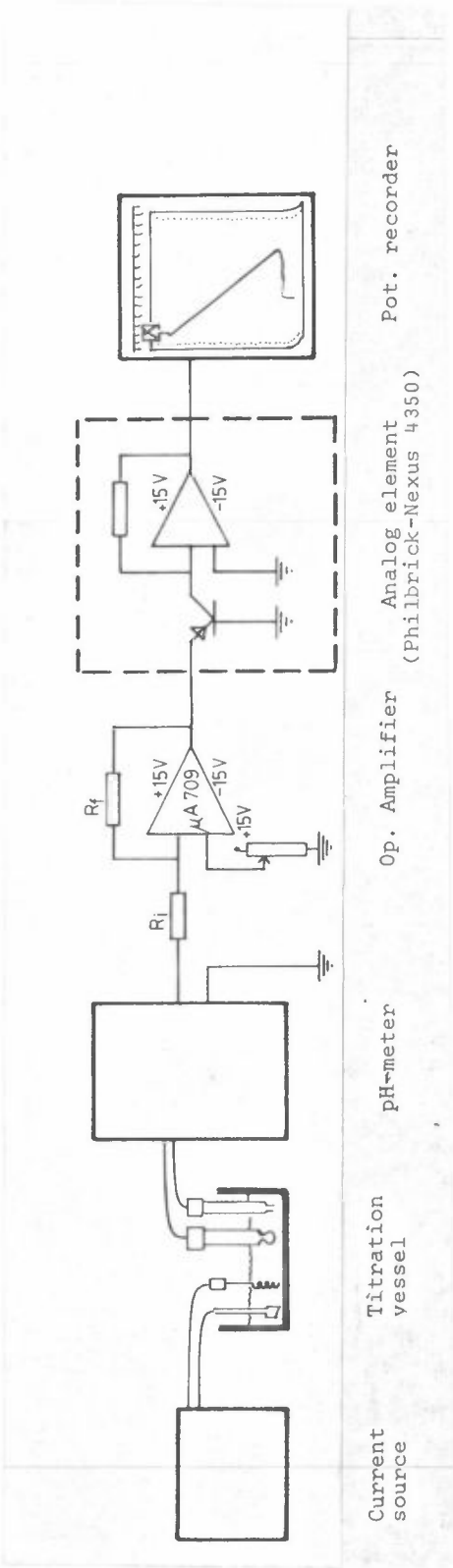


Figure A1

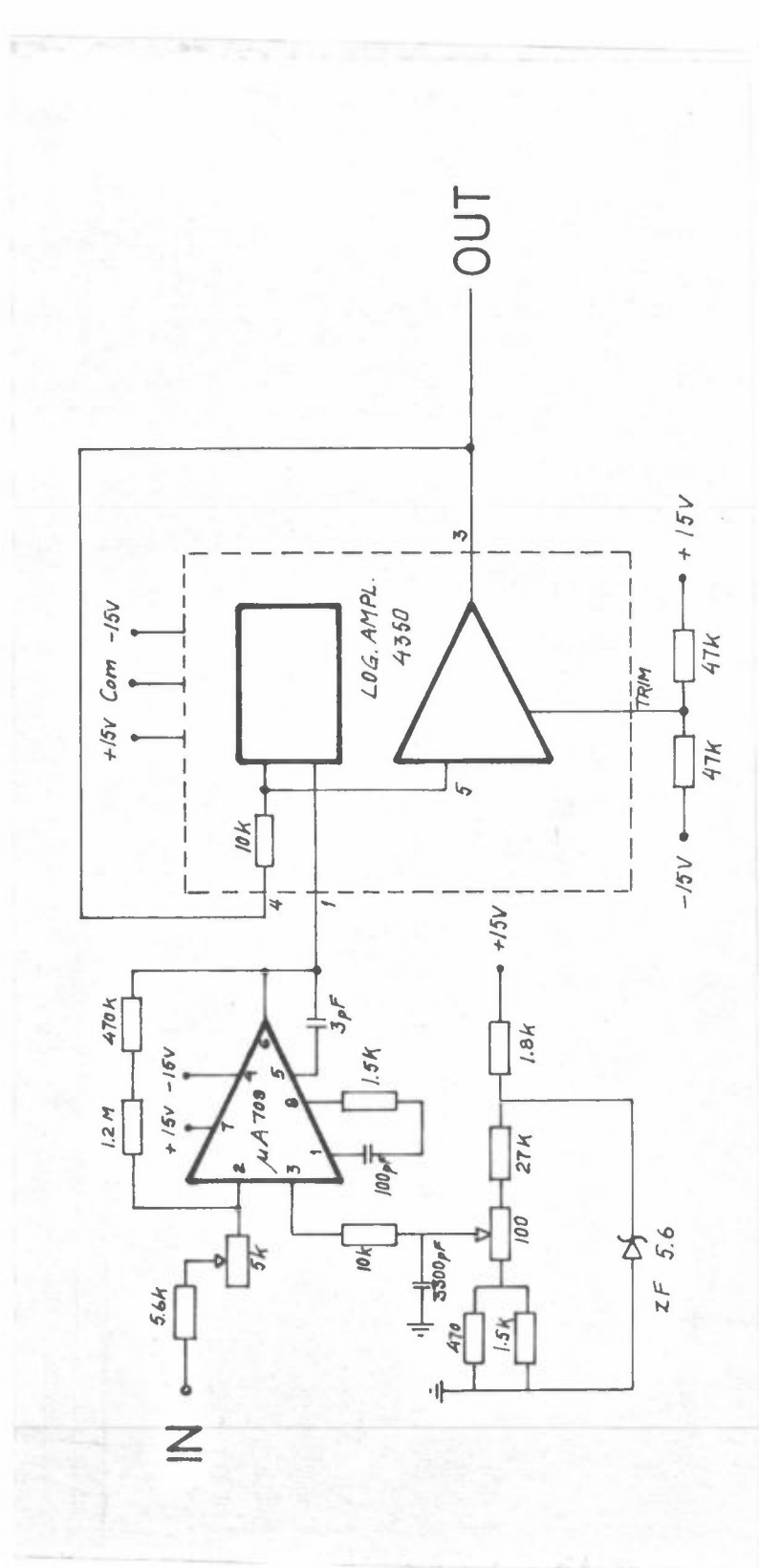


Figure A2.

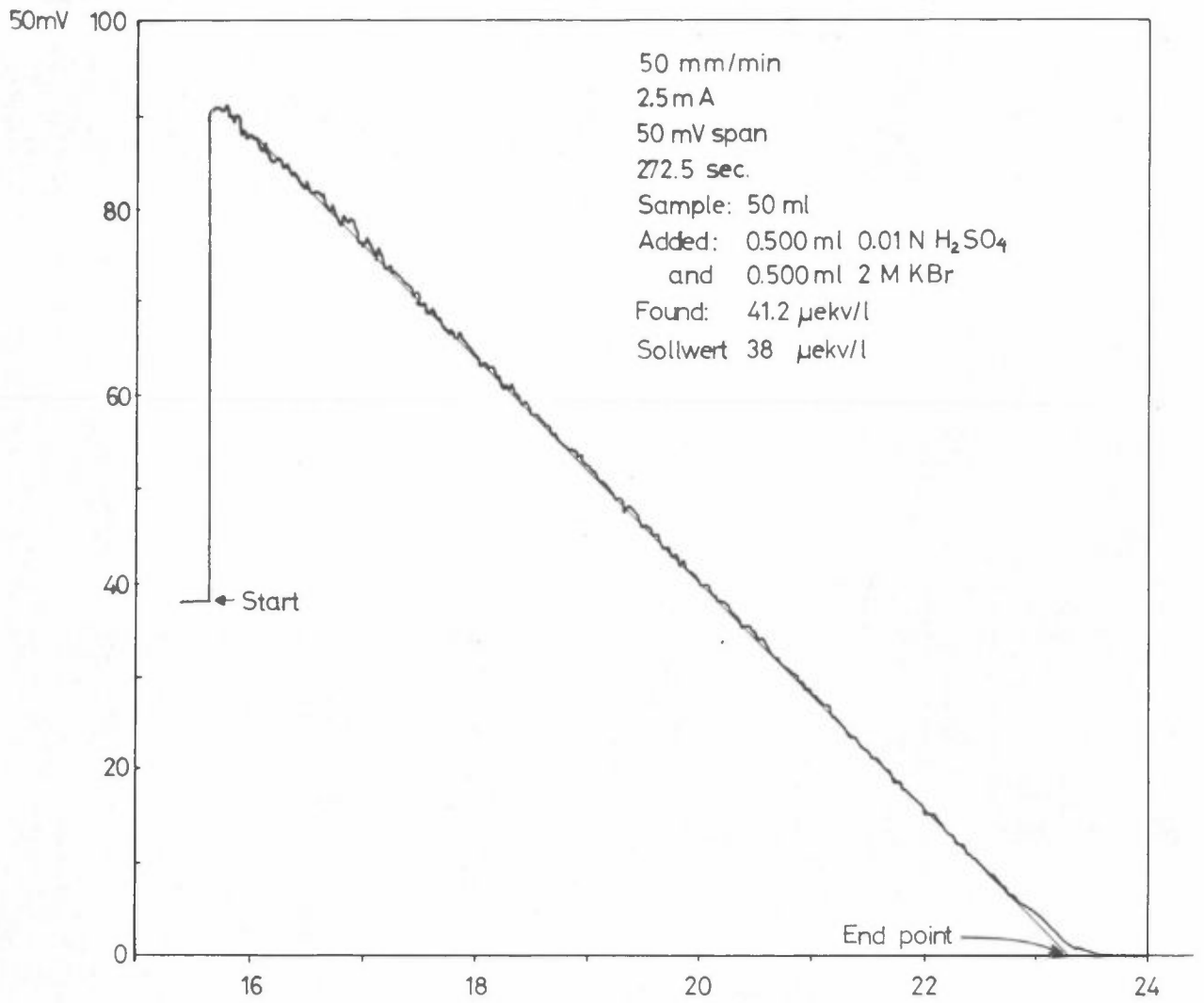


Figure A3.