# GOVERNMENT OF INDIA
# ATOMIC ENERGY COMMISSION

WATER CHEMISTRY STUDIES X – CONTINUOUS MONITORING OF
CHLORIDE ION CONCENTRATION IN THE RANGE 10–500 P.P.M.
USING A SPECIFIC ION ELECTRODE

*by*

S. V. Narasimhan and K. S. Venkateswarlu
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BHABHA ATOMIC RESEARCH CENTRE
BOMBAY, INDIA
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ABSTRACT

The continuous measurement of the concentration of chloride ions ($Cl^-$) in a flowing stream of aqueous solution, by an ion selective electrode is described in this report. The study was made under four different flowrates, namely, 50, 100, 150 and 200 ml/min. The measurements were fast and reproducible with the teflon electrode cell specially made for this purpose.

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1. INTRODUCTION

Ion selective electrodes, which are finding increasing applica-
tion in analytical potentiometry, measure directly the activity of the ion
of interest with minimum interference from many other ions. As the name
indicates, they are selective to a particular ion. In view of the importance
of chloride measurement on a continuous basis in several reactor water
systems, it was thought desirable to develop a procedure for this anion.

A liquid ion-exchange membrane electrode is one among the
different types of ion selective electrodes. One such electrode is
pictorially represented in fig.1. The solution, $a_1$, develops a potential
at the solution-membrane interface I. Similarly $a_2$ develops a potential
at the other membrane-solution interface II. The difference between these
two interface potentials is sensed by the internal reference Ag/AgCl
electrode. The electrical contact between $a_1$ and $a_2$ is maintained by
transport of the ion of interest across the membrane. The liquid ion
exchange membrane is a thin film of water insoluble, ion selective organic
liquid ion exchanger. The potential registered by the electrode is given
by the equation (1).

$$E = E_o - \frac{2.303 \ RT}{F} \quad \log a \qquad \qquad .. \ (1)$$

where  $E$ = the emf of the cell

$E_o$ = a constant equal to E when $a = 1$

$a$ = activity of the ion of interest

$R$ = gas constant

$T$ = Temperature in °K

$F$ = Faraday = 96495 coulombs.

The chloride ion selective electrode shows Nernstian behaviour in the range $1M - 2x10^{-4}M$. From equation (1), at $300°K$, for a ten fold change in activity of the chloride ion (for all univalent ions) the ion selective electrode gives approximately 58 $mV$ change in potential. This large change in potential can be utilised to monitor continuously the chloride ion activity. Since it is easier to handle molarity or p.p.m. than activity, the results of the following experiments are presented in p.p.m.

2. EXPERIMENTAL

Chloride ion selective electrode of liquid ion exchange membrane type, model 92-17 supplied by Orion Research Inc., was made use of in the present study. The double junction reference electrode, also supplied by the same company was used. The ion selective electrode was filled* one day before the start of the experiment and conditioned for 24 hours in 0.1M NaCl

. Solutions of NaCl 9.2, 53.2, 212.7 and 425.5 p.p.m. were prepared by diluting a standard $10^{-1}M$ NaCl solution.

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* It was found that commercially available and cheap Aliquot 336 (Tri-caprylylmethylammonium chloride) in isodecanol serves as a good liquid anion exchanger.

The electrode cell was made out of a teflon block (fig.2). The cell was so constructed that the tips of the indicator as well as the reference electrodes just touched the solution flowing through the cell. The inlet was arranged in such a way that the solution was sensed by the electrode the moment it entered the cell. The reference and the indicator compartment volumes were kept to a minimum.

The specific ion meter Model 407 was used in the study, which registered the potential sensed by the electrodes and which at the same time gave an output that could be recorded on an XY recorder. The meter selector knob was kept in "mv(exp.)" position. The calibration control knob was adjusted for a $10^{-3}$M solution of NaCl so that the meter showed zero deflection.

The recorder used was a three pen recorder Model B-34 Electronic Recorder RDK. The attenuator knob of the recorder was kept in 20 mV position full scale, with centre zero adjustment. Chart speed was adjusted to 60 mm/min.

The entire flow system (fig.3) was constructed out of either tygon or glass tubes. The reservoirs used were of 2 litres capacity Corning aspirator bottles.

The rotometer used in this study was constructed with a stainless steel ball and calibrated by collecting a fixed volume of liquid (500 ml) for various amounts of time in different positions of the stainless steel ball. The calibration graph is shown in fig.4.

The flowrates chosen for this study were 50, 100, 150 and 200 ml/min.

## 3. RESULTS

Each solution was passed till a constant baseline was obtained and then suddenly with a system of stopcocks a solution of another concentration was let in, while the flow of the previous solution was stopped. Enough time was allowed to get the baseline. Similarly various combinations listed in Table I were carried out. The graphs obtained are reproduced in fig.5-11. All graphs were analysed and the risetimes (10% to 90% change in potential) were calculated. These values are plotted against respective flowrates (fig.5a-10a). The slopes of these lines are listed in Table II. The slopes $(ml/\underline{ml}mt^{-1} = mt)$ are proportional to risetimes; therefore comparison of these slopes is equivalent to comparing risetimes for fixed flowrates.

## 4. CONCLUSION

The following conclusions can be drawn from this study:

1. For any change in concentration, the electrode response is almost instantaneous. This is an important and useful characteristic.

2. The system stabilises to the new concentration in less than 60 sec. The risetime, defined as the time taken for rise or fall in potential from 10 to 90% is less for a positive concentration change than for the same negative concentration change. This is true for any flowrate.

3. For either positive or negative concentration change, the risetime is independent of flowrate.

4. For a fixed flowrate, the risetime increases with increase in magnitude of the change in concentration of the chloride ion.

5. The system can be easily adopted to the requirements of reactor water systems.

TABLE I

| Initial concn. flowing p.p.m. | Change over to the concn. p.p.m. | Flowrate ml/min. | For 10% to 90% change | |
|---|---|---|---|---|
| | | | Time(sec.) | Vol.of soln. passing(ml) |
| 425.5 | 212.7 | 200 | 35 | 117 |
| | | 150 | 35 | 88 |
| | | 100 | 35 | 60 |
| | | 50 | 46 | 38 |
| | 53.19 | 200 | 58 | 190 |
| | | 150 | 55 | 137.5 |
| | | 100 | 55 | 92 |
| | | 50 | 55 | 46 |
| | 9.219 | 200 | 60 | 200 |
| | | 150 | 42.5 | 105 |
| | | 100 | 51.0 | 90 |
| | | 50 | 49.0 | 41 |
| 212.7 | 53.19 | 200 | 59.5 | 198 |
| | | 150 | 59 | 148 |
| | | 00 | 59 | 99 |
| | | 50 | 37 | 47.3 |
| | 9.219 | 200 | 52.5 | 175 |
| | | 150 | 53.0 | 132.5 |
| | | 100 | 48.0 | 80.0 |
| | | 50 | 40.0 | 33.3 |
| 53.19 | 9.219 | 200 | 31.0 | 100 |
| | | 150 | 40.0 | 100 |
| | | 100 | 29.0 | 48.3 |
| | | 50 | 29.0 | 24.2 |
| 9.219 | 53.19 | 200 | | |
| | | 150 | 24 | 60 |
| | | 100 | 29 | 48.4 |
| | | 50 | 24 | 20 |
| | 212.7 | 200 | 32 | 106 |
| | | 150 | 29 | 72.5 |
| | | 100 | 30 | 50.0 |
| | | 50 | 29 | 24.2 |
| | 425.5 | 200 | 48 | 160 |
| | | 150 | 41 | 102.5 |
| | | 100 | 37 | 62.0 |
| | | 50 | 34 | 28 |
| 53.19 | 212.7 | 200 | 44 | 147 |
| | | 150 | 40 | 100 |
| | | 100 | 40 | 67 |
| | | 50 | 39 | 32 |
| | 425.5 | 200 | 53 | 174 |
| | | 150 | 45 | 112.5 |
| | | 100 | 36 | 60 |
| | | 50 | 30 | 25 |
| 212.7 | 425.5 | 200 | 35 | 117 |
| | | 150 | 35 | 88 |
| | | 100 | 38 | 60 |
| | | 50 | 38 | 32 |

## TABLE II

| Initial concn. flowing p.p.m. | Change over to concn. p.p.m. | Slope(mt) |
|---|---|---|
| 425.5 | 212.7 | 0.51 |
| | 53.2 | 0.94 |
| | 9.2 | 1.025 |
| 212.7 | 53.2 | 0.98 |
| | 9.2 | 0.97 |
| 53.2 | 9.2 | 0.51 |
| 9.2 | 53.2 | 0.425 |
| | 212.7 | 0.51 |
| | 425.5 | 0.89 |
| 53.2 | 212.7 | 0.72 |
| | 425.5 | 0.83 |
| 212.7 | 425.5 | 0.51 |

Ag/AgCl Electrode

CHLORIDE SOLUTION OF
CONSTANT ACTIVITY $a_1$

LIQUID ION EXCHANGER
SUPPORTED ON A POROUS
INERT MEMBRANE

CHLORIDE SOLUTION OF
VARYING ACTIVITY $a_2$

I

II
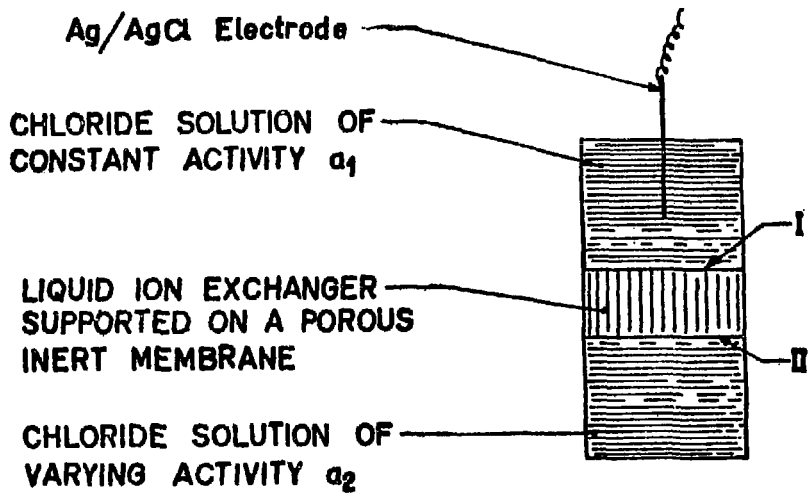
FIG. 1.
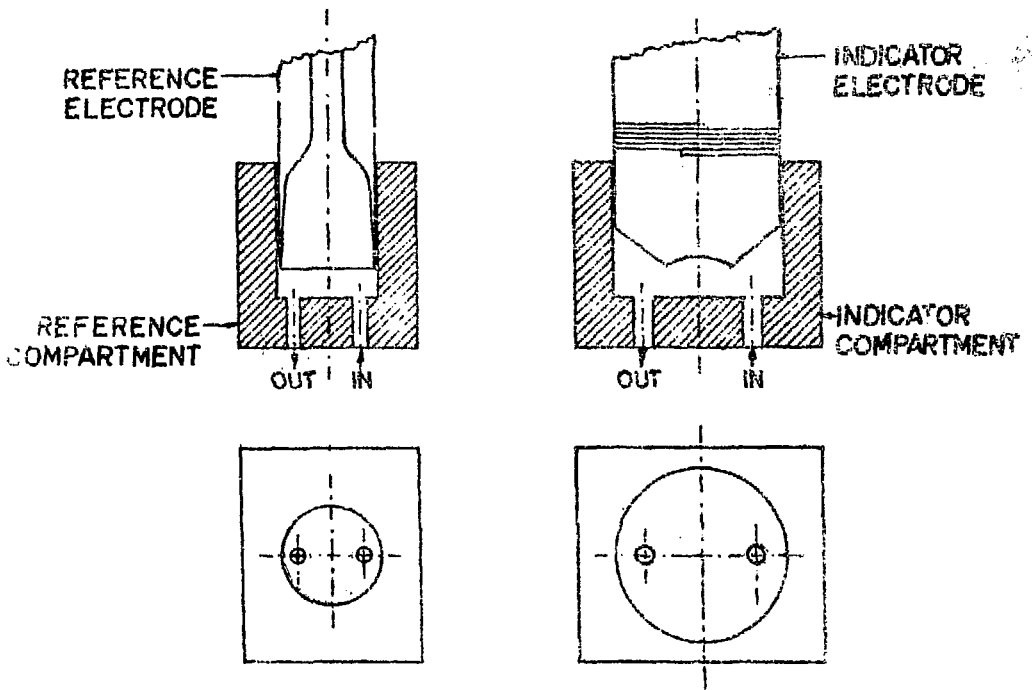
FIG. 2. THE ELECTRODE CELL.



INDICATOR ELECTRODE
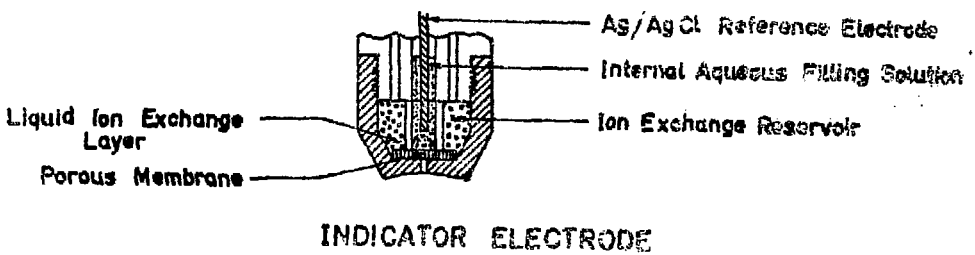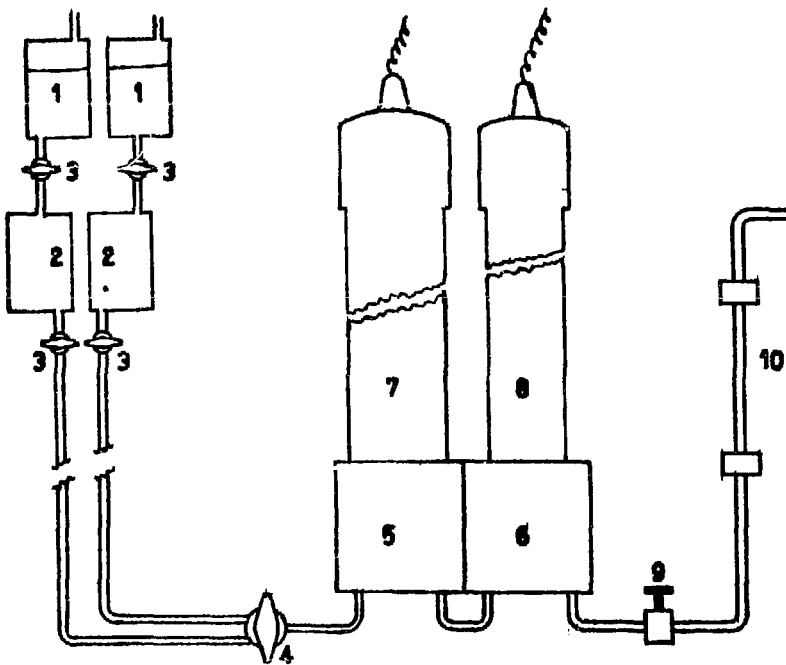
Legend:

1 - Solution reservoirs.

2 - Constant height, constant level reservoir.

3 - Stop-cocks.

4 - Two way stop-cock.

5 - Indicator electrode compartment.

6 - Reference electrode compartment.

7 - Indicator electrode.

8 - Reference electrode.

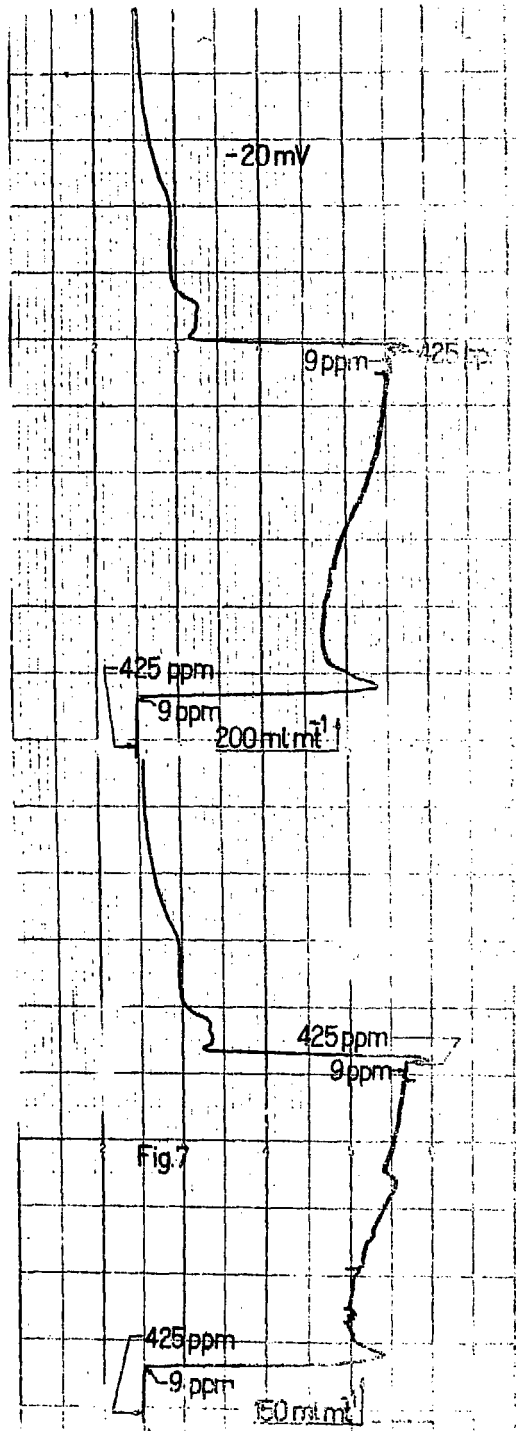9 - Flow-rate control valve.

10 - Rotameter.

Fig. 3. FLOW SYSTEM

Fig.4. Flow-rate calibration.
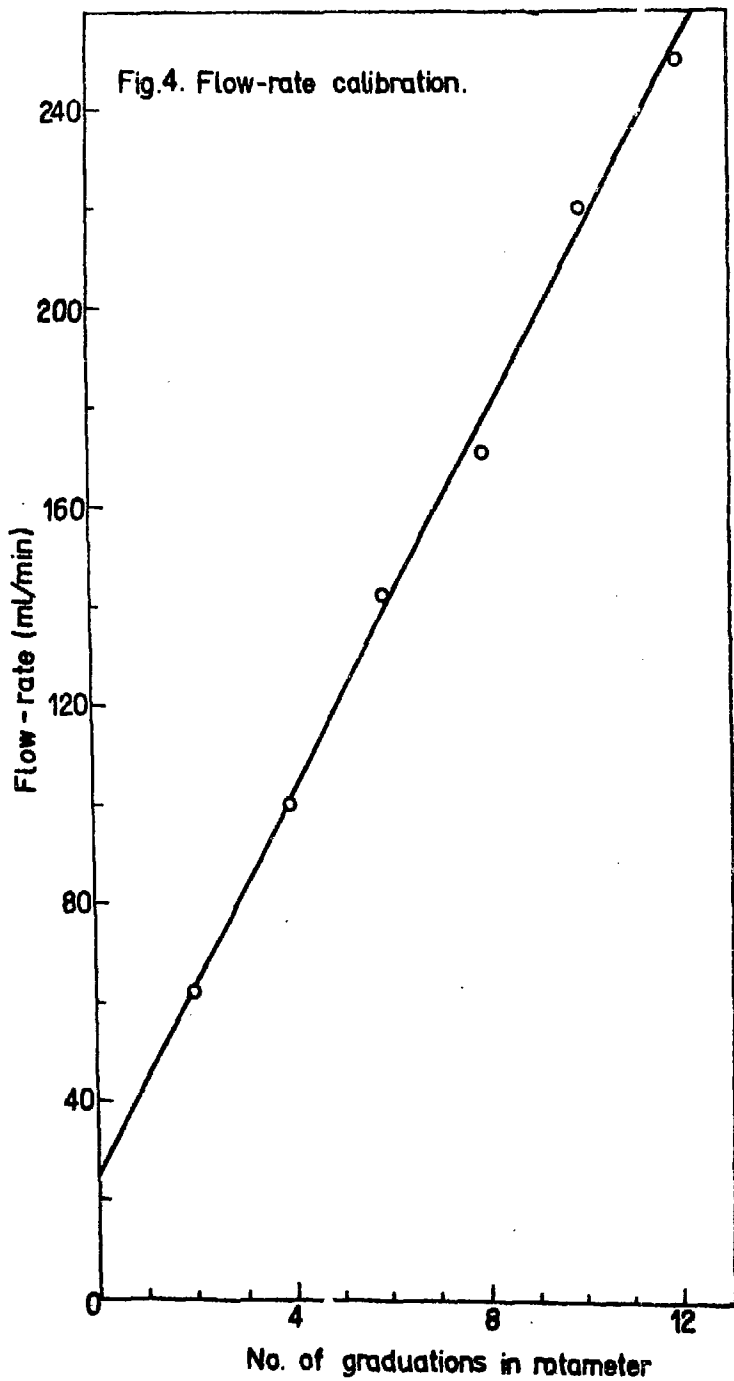
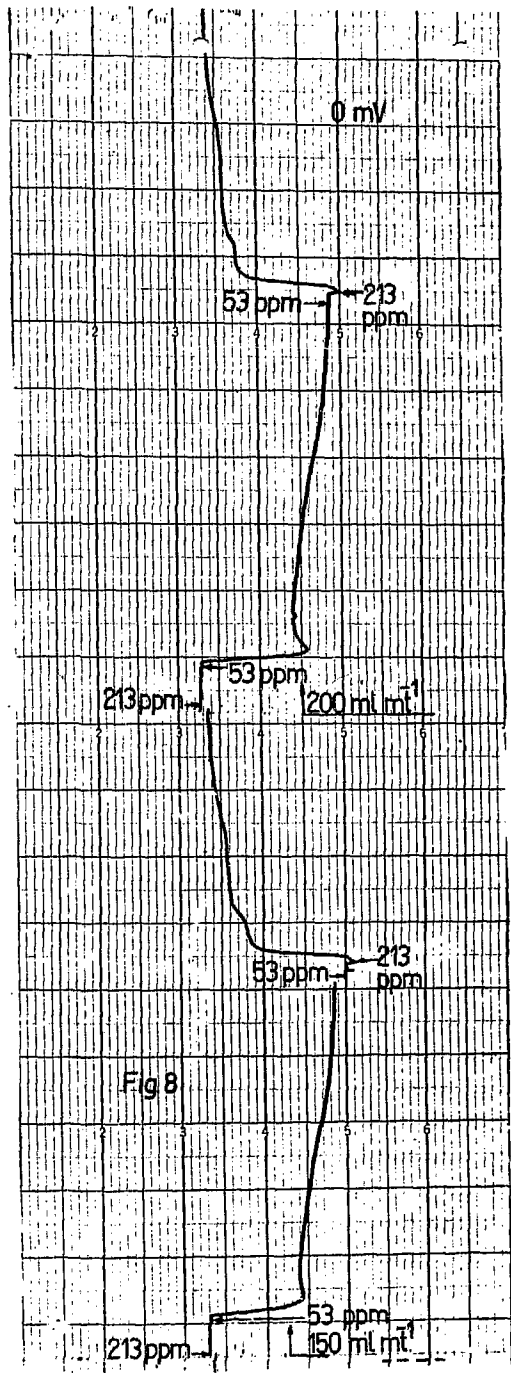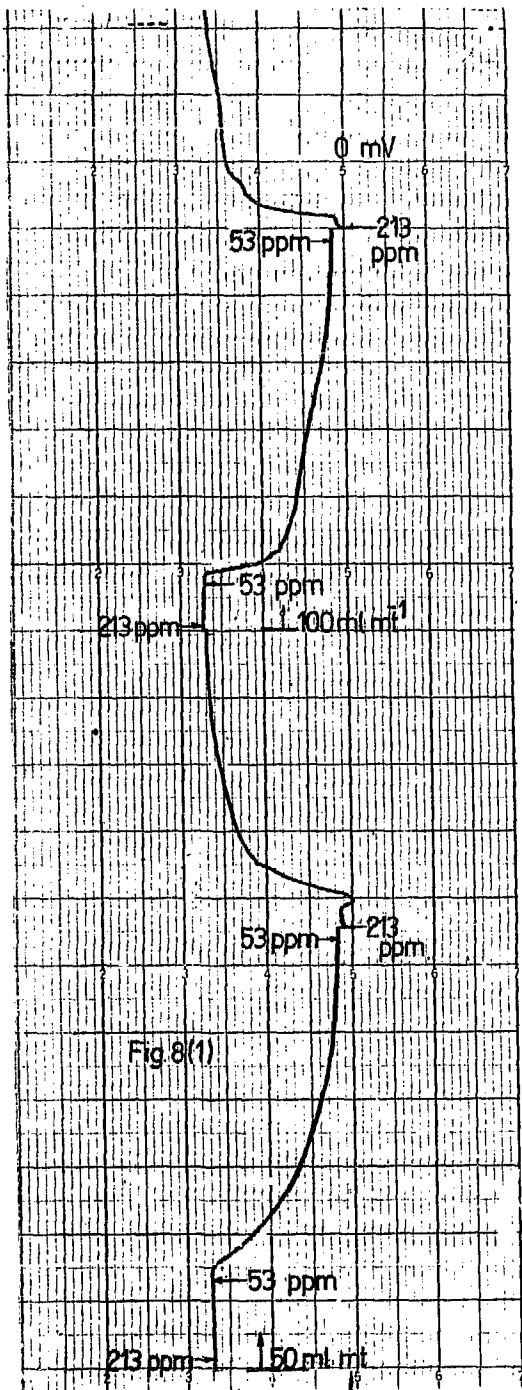## Appendix


## Reading of fig. nos. 5 to 10.


The movement of the chart always starts at the bottom of
the paper and goes up. An arrow from the left indicates that
specified concentration is flowing to start with. An arrow from
the right indicates that the original flow is stopped and a new
concentration is being introduced. This is true for each flowrate
which is also marked on the graph.


Scale:   Y axis  =  Time (1 cm = 20 sec.)

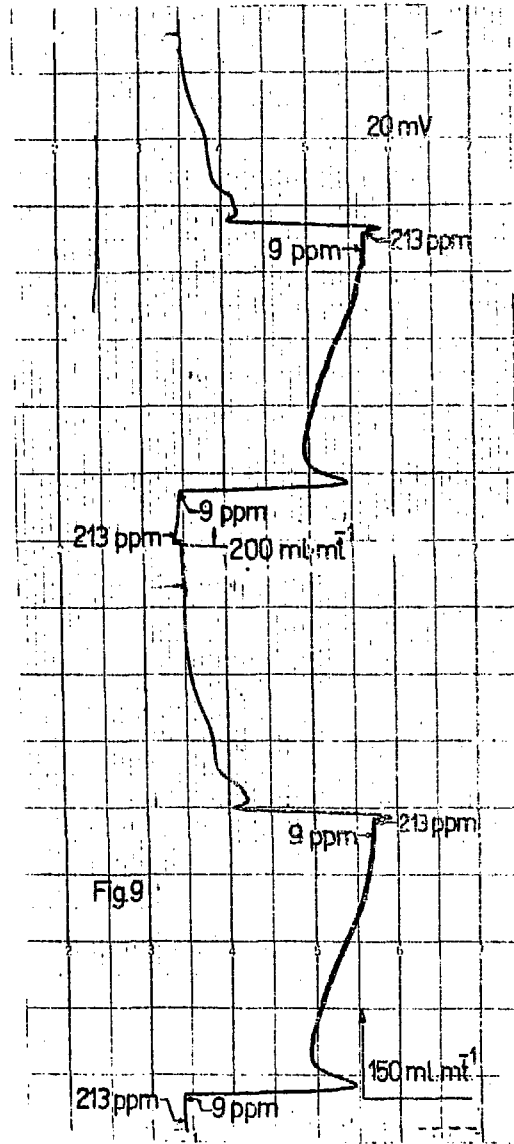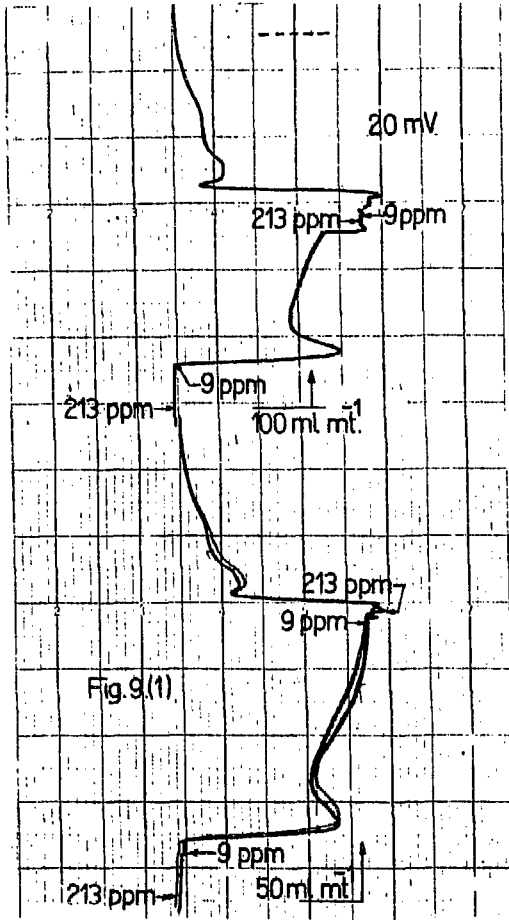         X axis  =  mV   (1 inch = 40 mV)

-40 mV

$10^3$

100 nl mt$^{-1}$    53ppm    425 ppm

425 ppm — 53 ppm

Fig 5(1)

50 ml mt$^{-1}$    53ppm    425 ppm



-40 mV

425 ppm    53 ppm

425 ppm

200 ml mt$^{-1}$    53 ppm    425 ppm

425 ppm    53 ppm

Fig 5

150 ml mt$^{-1}$    53 ppm    425 ppm

213 ppm — 425 ppm

213 ppm

425 ppm — 200 ml mı̄

425 ppm

−60mV

Fig.6

213 ppm

425 ppm — 150 ml mı̄⁻¹

.contd.

−20 mV

213 ppm — 425 ppm

213 ppm

425 ppm — 100 ml mı̄⁻¹

213 ppm — 425 ppm

Fig.6(1)

213 ppm

425 ppm — 50 ml mı̄⁻¹

Fig 7 (1)

0 mV

425 ppm
9 ppm

425 ppm
9 ppm
100 ml ml$^{-1}$

425 ppm
9 ppm

425 ppm
9 ppm
50 ml ml$^{-1}$

Fig. 7

−20 mV

9 ppm ⌐425 ppm

425 ppm
9 ppm
200 ml ml$^{-1}$

425 ppm
9 ppm

425 ppm
9 ppm
50 ml ml$^{-1}$

Fig 8(1)

Fig 8

0 mV

53 ppm
213 ppm

53 ppm
213 ppm → 100 mL mt⁻¹

53 ppm
213 ppm

53 ppm

213 ppm → 50 mL mt⁻¹

0 mV

53 ppm
213 ppm

213 ppm → 53 ppm
200 mL mt⁻¹

53 ppm
213 ppm

53 ppm

213 ppm → 150 mL mt⁻¹

Fig. 9.(1)



Fig. 9

40 mV

53 ppm   9 ppm

9 ppm

150 ml/mt

53ppm

53 ppm

9 ppm

9 ppm

100 ml mt

Flg 10 1)

53ppm

20 mV

53 ppm

9 ppm

9 ppm

150 ml mt

Fig 10

53ppm

53 ppm

9 ppm

9 ppm

200 ml mt

53ppm

Fig. 5a - 10a.


Plot of volume of liquid flushed out when there is
a change in concentrations (in the rise time)

vs

flowrate.

Shaded points refer to higher to lower concentration
change.

Nonshaded points indicate lower to higher concentra-
tion change.
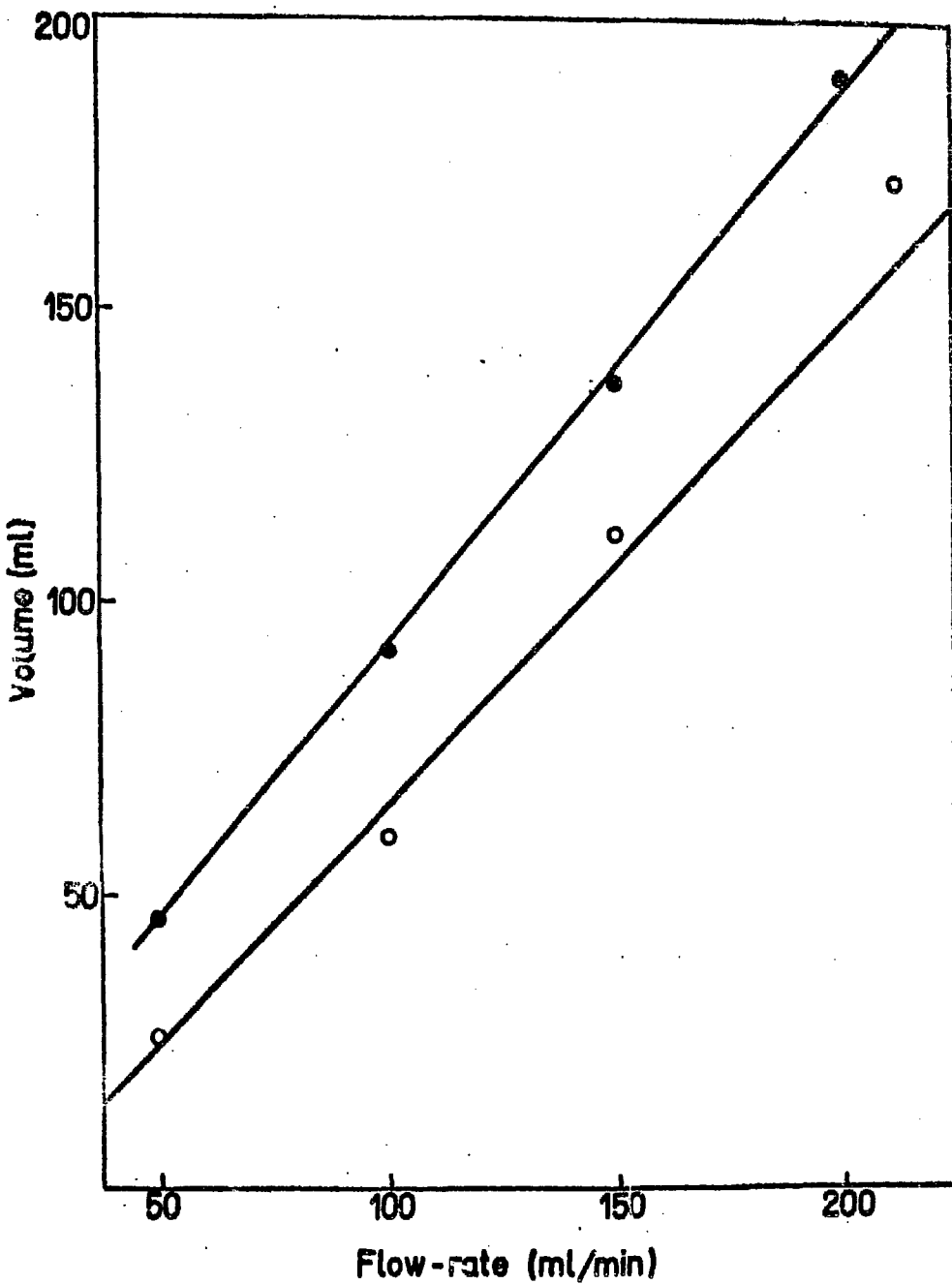
Fig 5a   53 ppm ⇌ 425 ppm
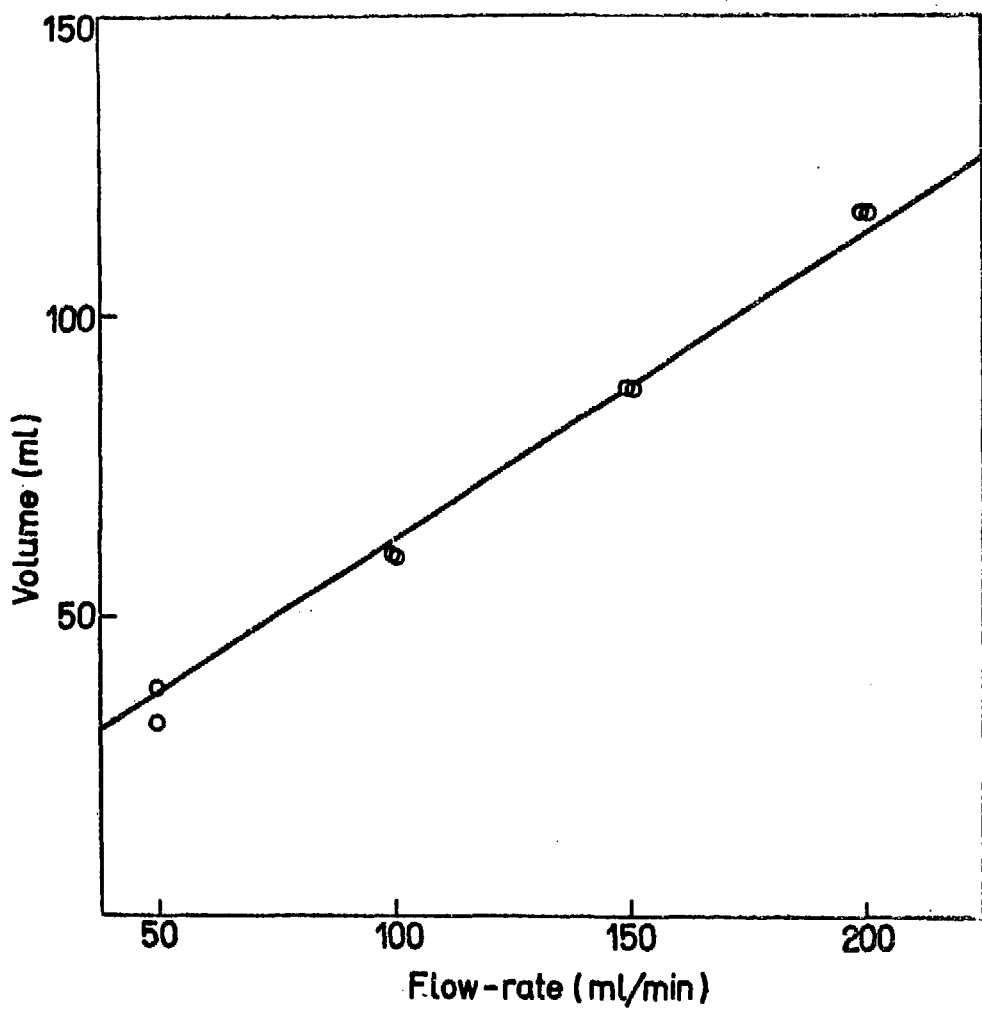
Fig.6a. 213 ppm ⇌ 425 ppm
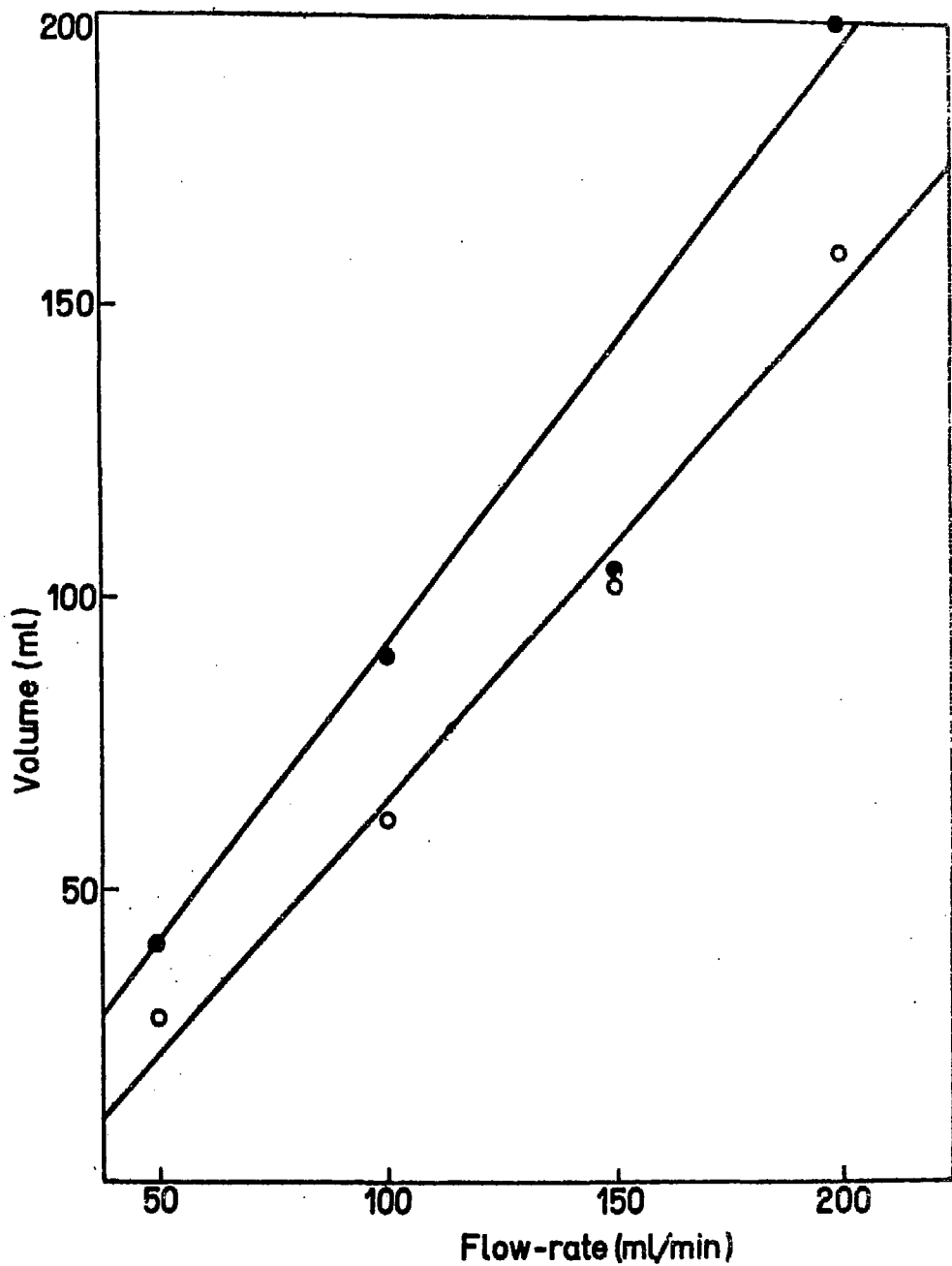
Fig. 7a  9ppm ⇌ 425ppm
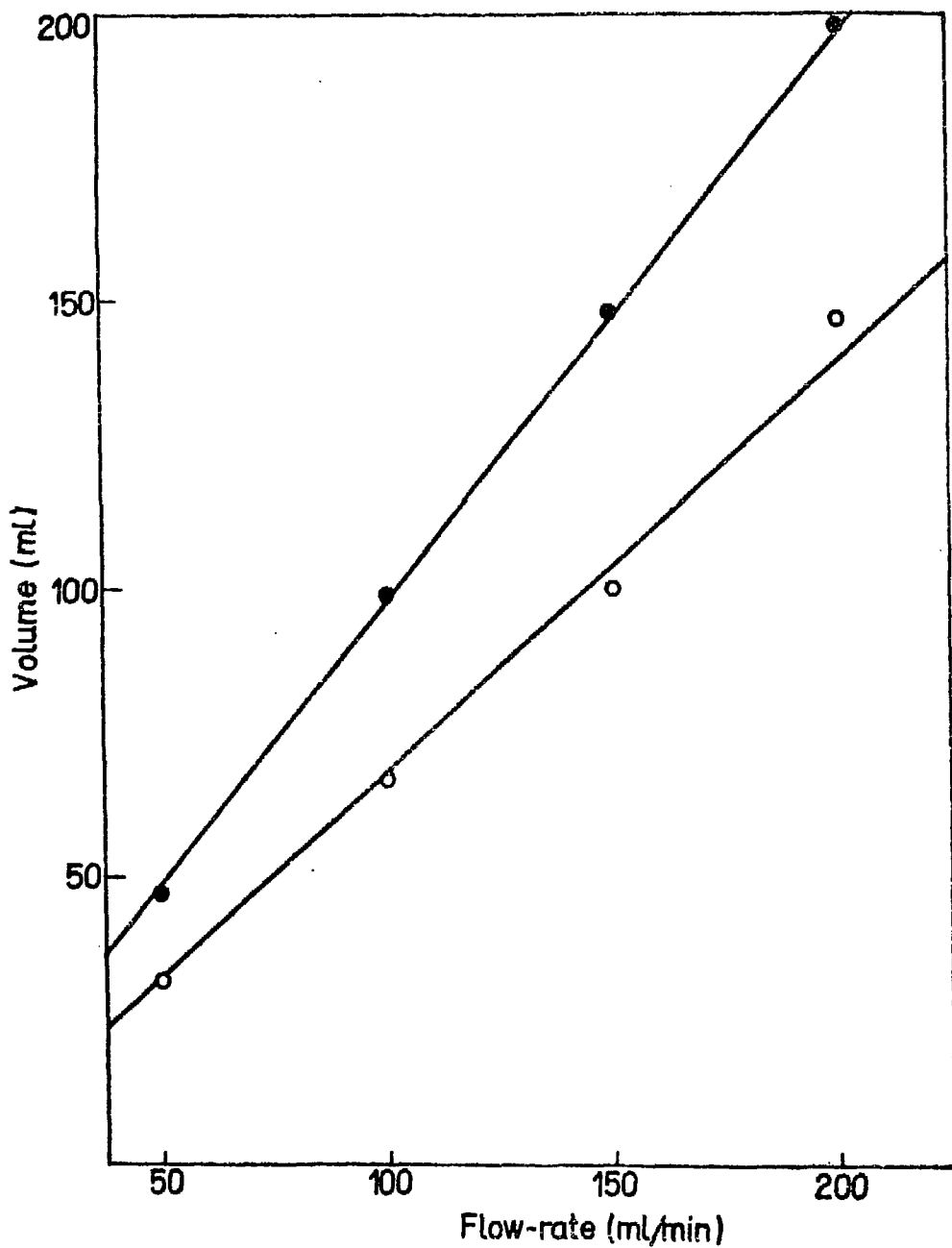
Fig. 8a. 53 ppm ⇌ 213 ppm
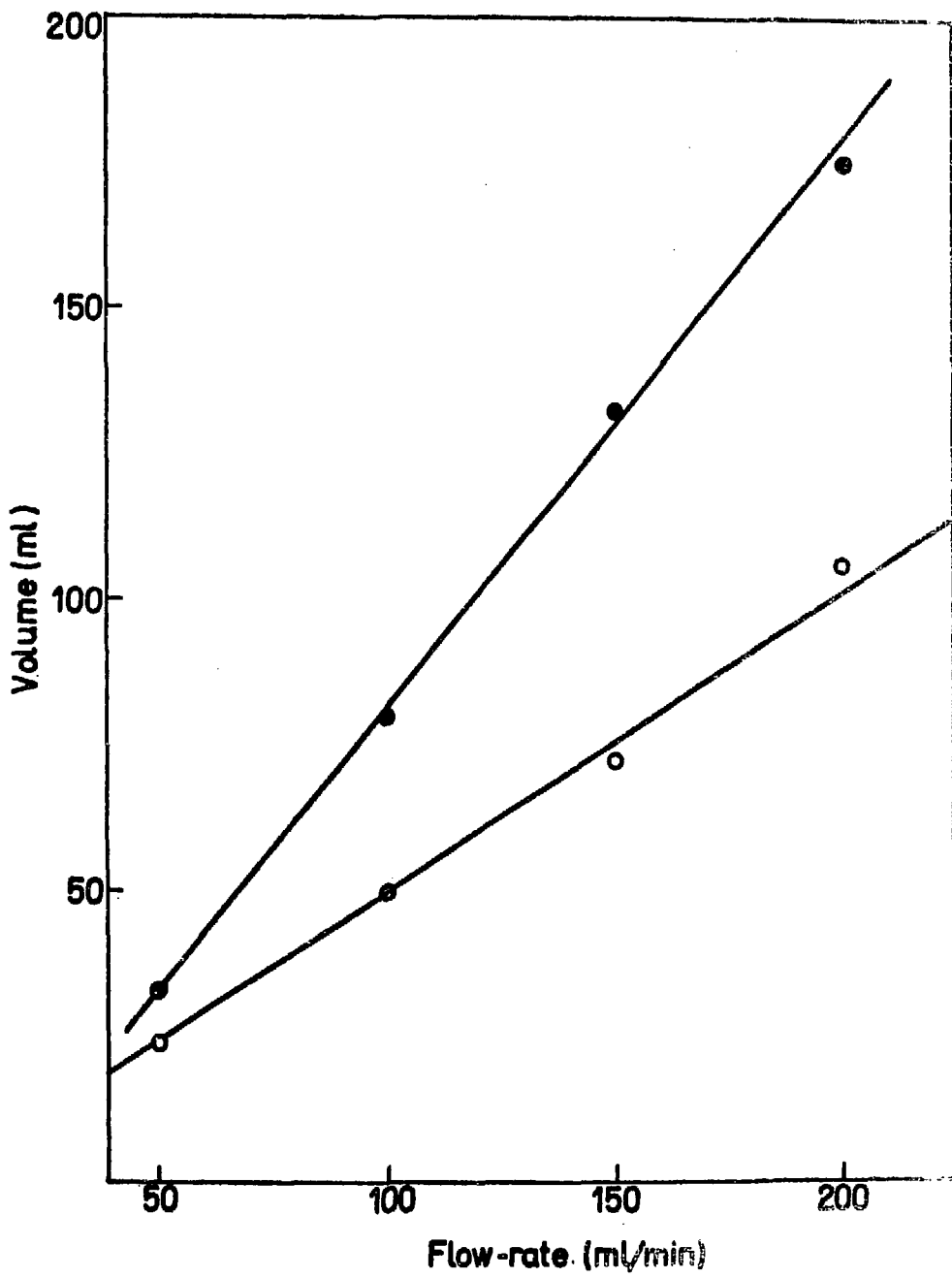
Fig. 9a    9 ppm ≠ 213 ppm

Fig.10a    9 ppm ⇌ 53 ppm