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TECHNICAL DIVISION
SAVANNAH RIVER LABORATORY

DPST-82-677

Acc. NO. 148752

CC: J. P. Moseley, Wilm
J. R. Hilley, SRL
S. Mirshak
J. A. Kelley
R. M. Wallace
E. L. Albenesius
J. F. Ortaldo
M. D. Boersma
F. H. Brown
M. A. Ebra
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D. D. Walker
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MEMORANDUM

July 6, 1982

TO: R. B. FERGUSON

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FROM: L. L. KILPATRICK

L L Kilpatrick

CESIUM REMOVAL FROM SYNTHETIC SUPERNATE USING DUOLITE CS-100

INTRODUCTION

This document describes a laboratory tracer facility which was used to show Duolite CS-100 resin's capability for removing cesium from supernate. The data presented is part of the High Level Waste Technology Section's effort to develop design information for the Reference Defense Waste Processing Facility (DWPF).

BACKGROUND

About 20 million gallons of high level radioactive waste, generated in the production of special nuclear materials during the last twenty-five years, are stored in large underground tanks at the Savannah River Plant in the form of a damp salt cake and a gelatinous sludge. A process was being developed^{1,2,3,4,5} to: (1) remove from supernate the hazardous radionuclides, (2) recombine radionuclides with sludge, and (3) combine sludge in leach resistant glass matrix suitable for long-term geologic storage. A step in this conceptual process is the use of an ion exchange resin to remove cesium from the supernate.

SUMMARY

A tracer facility (Figure 1,2) for testing ion exchange resins was built and used to test Duolite CS-100 resin's capability to remove cesium from synthetic supernate. Cesium-137 was used as a tracer. The variables, feed flow rate, and cesium concentration were plotted as functions of, % change of cesium concentration to column volumes passed (Appendix A). The resultant K_d 's were then plotted as a function of cesium concentration (Figure 3). The K_d data was then extrapolated to other hydroxide cesium concentrations, (Appendix B).

At a DF of 10,000, the relationship of feed flow rate was correlated to column volumes passed and cesium concentration (Figure 4).

The physical properties of the resin are shown in Appendix C.

I/E TRACER LEVEL FACILITY (TLF) EQUIPMENT

The major goals of this equipment were to demonstrate the proposed DWPF flowsheet and to explore the I/E variables such as feed rate, elutriant composition, and regenerant composition.

The height of the cesium I/E resin column (92 inches) was near the expected DWPF column height. A three inch diameter column was chosen to meet the limits of radiation and maximum reasonable laboratory feed tank size (100 gal.). A schematic of the I/E test facility (ST5-22530), as installed in the laboratory (Room 139, Building 773-A), is shown in Figure 1. The facility includes: a glass I/E column, 100 gallon feed tank, receipt tank and automatic gamma counting sensors in column input and output streams.

Both columns were made of Corning beaded pressure pipe rated at 50 psig. The resin was supported by a perforated plate. A Johnson Profile wire screen (.007 inch slot) distributed the feed at the top of the column and prevented resin from entering the feed line during the backwash cycle.

A mix tank (30 gal. stainless steel) was used to make up elutriant and regenerant. Polyethylene carboys (50 liter) served as metering tanks for water, elutriant, and regenerant.

Two mRoy duplex positive displacement pumps (maximum flow 12.4 gph for load and 3.6 gph for elution and regeneration) supplied feeds to the column. Four Jabsco® self-priming impeller pumps (5.5 gpm at 10 ft. head) transferred liquids from drums, metering tanks, receipt tank, and floor pans.

Over-pressure protection was provided by 35 psig relief valves on the metering pumps and by 30 psig electrical pump overpressure interlocks that: shut off the pumps, fed the tank agitator, and sent an alarm to Building Operations. The pumps were also shut off by level switch/alarms that were activated if a pump ran dry or liquid spilled into a secondary floor container pan. See ST5-20550, 20552.

Because of the very low cesium-137 tracer concentration in the I/E effluent, automatic counting equipment and 3 inch sodium iodide detectors (in lead shielded counting chambers) were used. The I/E inlet feed chamber (44 ml) was made of a coiled 0.15 ID Teflon tube, and the effluent chamber (1000 ml) of teflon and polypropylene (SK 3620-LS). These plastics were used to reduce buildup of radionuclides on surfaces and thus reduce background levels and variations.

EXPERIMENTAL RESULTS

Duolite CS-100 resin (Lot 316-300-OE; 40-60 mesh U. S. standard) in the hydrogen form was loaded in the column and then converted to the sodium form with 0.5 molar NaOH. Spiked supernate was passed through the column (Table I, II, III and Appendix A) and the results tabulated (Table III, IV) and plotted (Figures 3,4). The results were then extrapolated (Appendix B) to other cesium and hydroxide levels (Figure 5).

The feed and first rinse cycles were downflow, and the elution and regeneration cycles upflow. After loading the resin in the column, it was treated with elutriant and regenerant. Gamma counting of the process streams was used to calculate the

R. B. FERGUSON

4

DPST-82-677
July 6, 1982

decontamination factor (DF) and the elution frequency. The down-flow feed rate tested was varied from 0.43 to 3.0 gpm/ft², and the upflow elution-regeneration rate tested was 0.54 gpm/ft². Elution of cesium was with .5 molar formic acid³ and regeneration with 0.5 molar NaOH.

The supernate pressure drop through resin is shown by Figure 19 in Appendix C.

LLK:pmc
Att
Disc 1

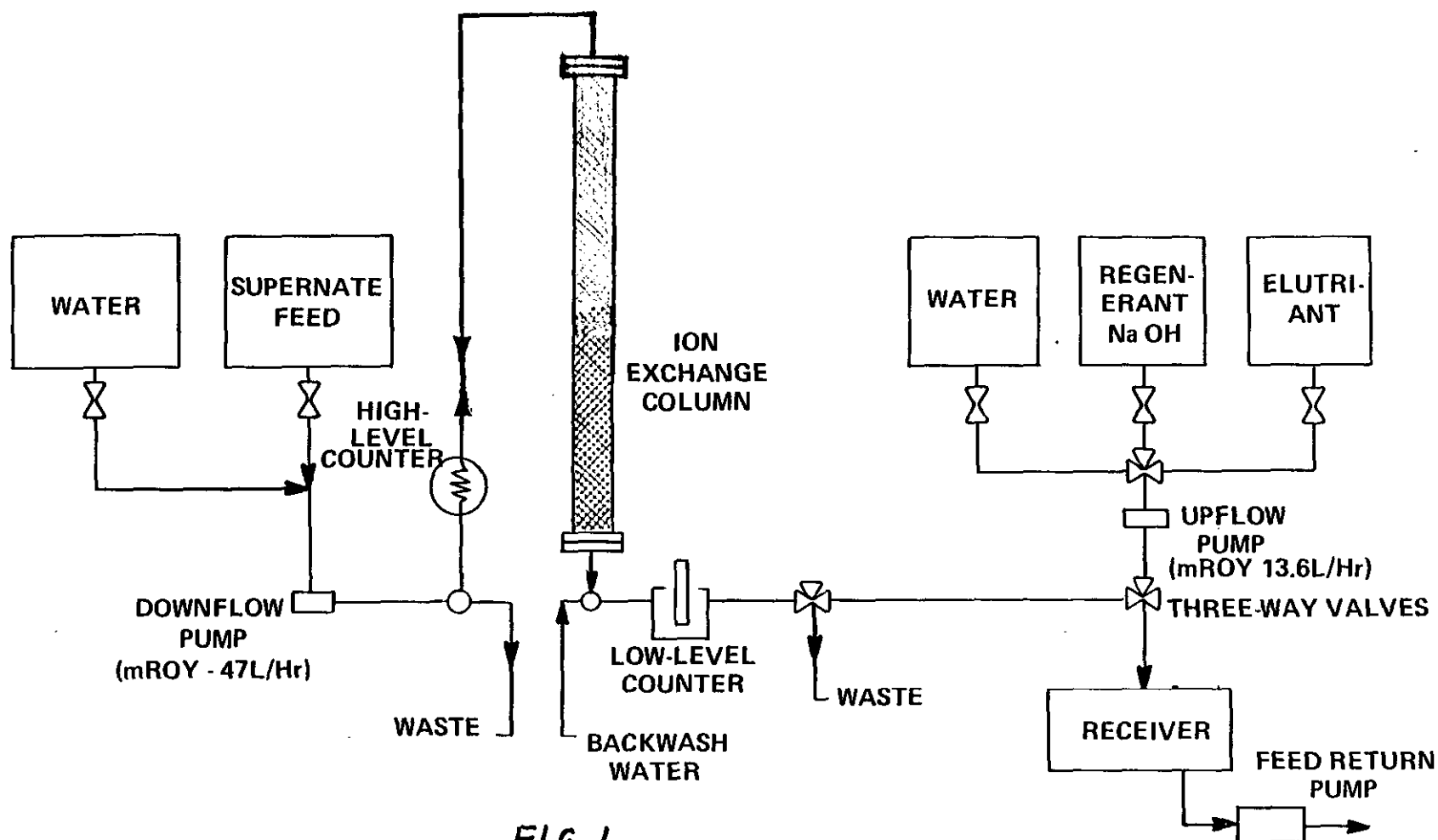


FIG 1

STRONTIUM TRACER LEVEL ION EXCHANGE FACILITY

Cs/Sr ION EXCHANGE TRACER FACILITY

FIG 2

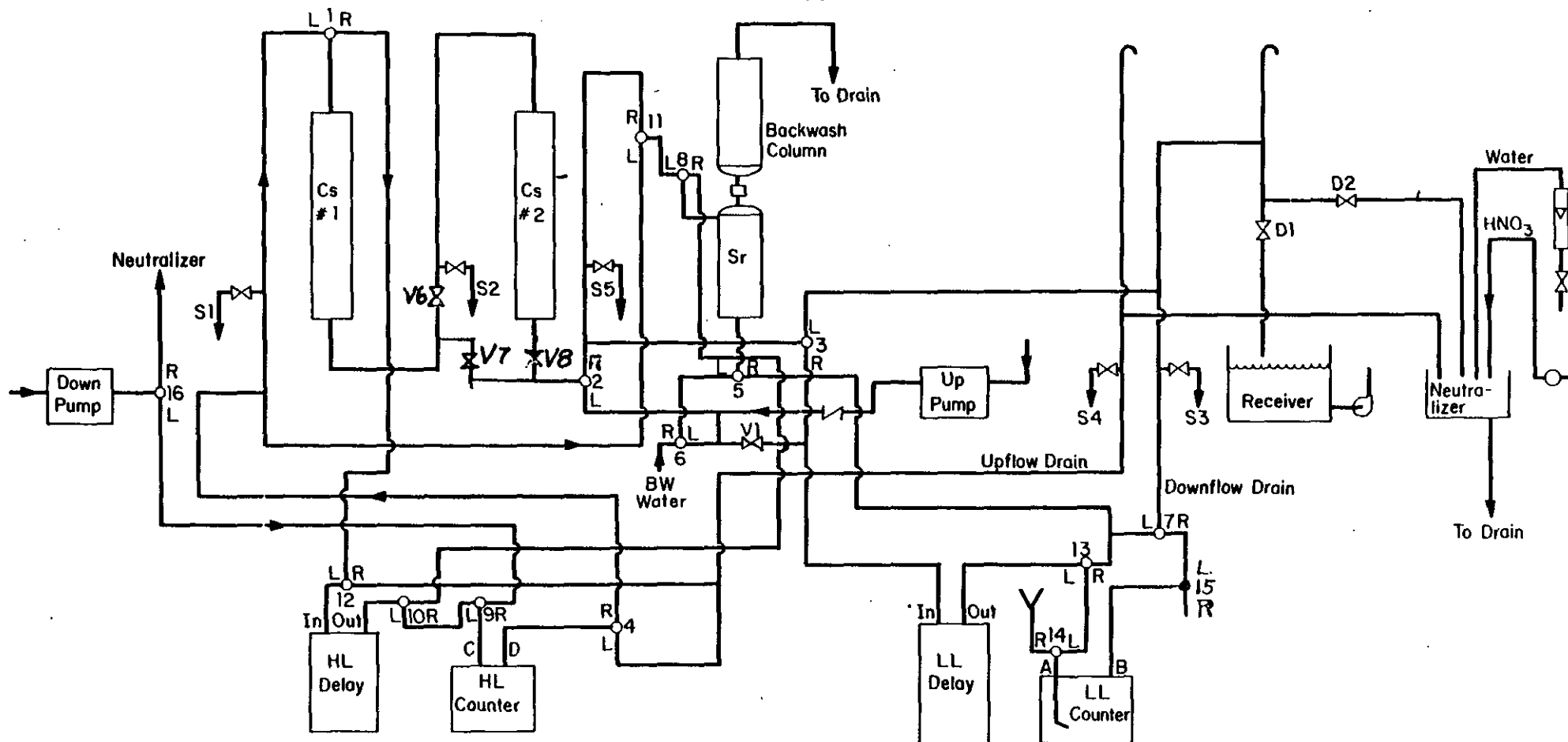


TABLE I

Synthetic Supernate Feed to Duolite CS-100 Ion Exchange Column

<u>Ion</u>	<u>\bar{M}</u>
AlO ₂	0.423
NO ₃	2.2
NO ₂	0.95
OH	1.62
CO ₃	0.48
SO ₄	0.24
Na	5.3

SpGr = 1.29

Dissolved Solids = 33%

TABLE II

CS-100 Experimental Range Attempted

<u>Item No.</u>	<u>Test No.</u>	<u>Range Expected K_d</u>	<u>C_s M</u>	<u>CV's/Hr</u>	<u>gpm/ft²</u>
1	4C	100	2.5E-4	1.7	1.33
2	5C	100	2.5E-4	3.8	2.97
3	6C	100	2.5E-4	.84	0.66
4	7C	50	2.5E-3	1.7	1.33
5	8C	50	2.5E-3	3.8	2.97
6	9C	50	2.5E-3	.84	0.66
7	10C	200	2.5E-5	1.7	1.33
8	11C	200	2.5E-5	3.8	2.97
9	12C	200	2.5E-5	.84	0.66

TABLE III

Distribution Coefficient (K_d) Measured at 60% Column
Breakthrough

Test No.	CV's/Hr	$\frac{Cs}{M}$	CV's @ 60% Breakthru	(1.1) CV's @ 60%	K_d See Below
1C	1.58	2.4E-4	35	38	89.3
2C	1.61	"	37	40.7	94.4
4C	1.66	"	32	35.2	81.7
5C	3.8	"	28	30.8	71.5
6C	.57	"	32	35.2	81.7
7C	1.55	2.5E-3	14	15.4	35.7
8C	2.13	"	14	15.4	35.7
9C	.51	"	14	15.4	35.7
10C	1.5	2.5E-5	40	44	102
11C	2.0	"	55	60.5	140
12C	.55	"	57	62.7	145

$$K_d = \frac{(1.1)(CV's @ 60\%)}{(0.431)} \approx [(-22.45 \ln Cs) - 103]; \text{ (Figure 3)}$$

$$\rho_B = 0.431 \text{ gms resin in } N_a \text{ form/ml resin in Na form in } 1M^-NaOH.$$

DISTRIBUTION COEFFICIENT (K_D)
FOR DUOLITE CS-100 (40-60 MESH)
VS CESIUM CONCENTRATION
IN SUPERNATE

FIGURE 3

ION	\bar{M}
OH	1.62
NO ₃	2.2
NO ₂	.95
AlO ₂	.423
CO ₃	.48
SO ₄	.29
K	.0095
Na	5.3

CS
MOLARITY

.004
.003
.002
.001
.0009
.0008
.0007
.0006
.0005
.0004
.0003
.0002
.0001
.00009
.00008
.00007
.00006
.00005
.00004
.00003
.00002

CESIUM
MOLARITY

.0001
.00009
.00008
.00007
.00006
.00005
.00004
.00003
.00002

$$K_D = \frac{(1.1)(CV's @ 60\% \text{ BREAKTHRU})}{P_B}$$

$$K_D = -22.45 \ln C_S - 103$$

$$P_B = \frac{\text{wt oven dried Na form}}{\text{Volume in 1M NaOH}} = 2.431$$

30 40 50 60 70 80 90 100 110 120 130 140 150
 K_D ~ DISTRIBUTION COEFFICIENT

TABLE IV

At DF = 10,000 Supernate Flow Rate vs. Column Volumes Fed At
Various Cesium Concentrations

<u>Test*</u>	<u>CsM</u>	<u>CV's</u>	<u>CV's/Hr</u>	<u>gpm/ft²</u>
8C	2.5E-3	21	2.13	1.66
7C	2.5E-3	23	1.55	1.21
	2.5E-3	41	.51	0.40
5C(2)	2.5E-4	10	3.8	2.97
4C	2.5E-4	18	1.66	1.30
2C	2.5E-4	19	1.61	2.56
1C	2.5E-4	21	1.58	1.32
6C	2.5E-4	26.5	.57	0.445
11C	2.5E-5	21	2.0	1.56
10C	2.5E-5	23	1.5	1.17
12C	2.5E-5	41	.55	0.43

*See Appendix A.

FOR DF=10000
SUPERNATE FLOW RATE VS
COLUMN VOLUMES FOR
VARIOUS CESIUM CONCENTRATIONS
FOR DUOLITE CS-100 (40-60 MESH)

FIGURE 4

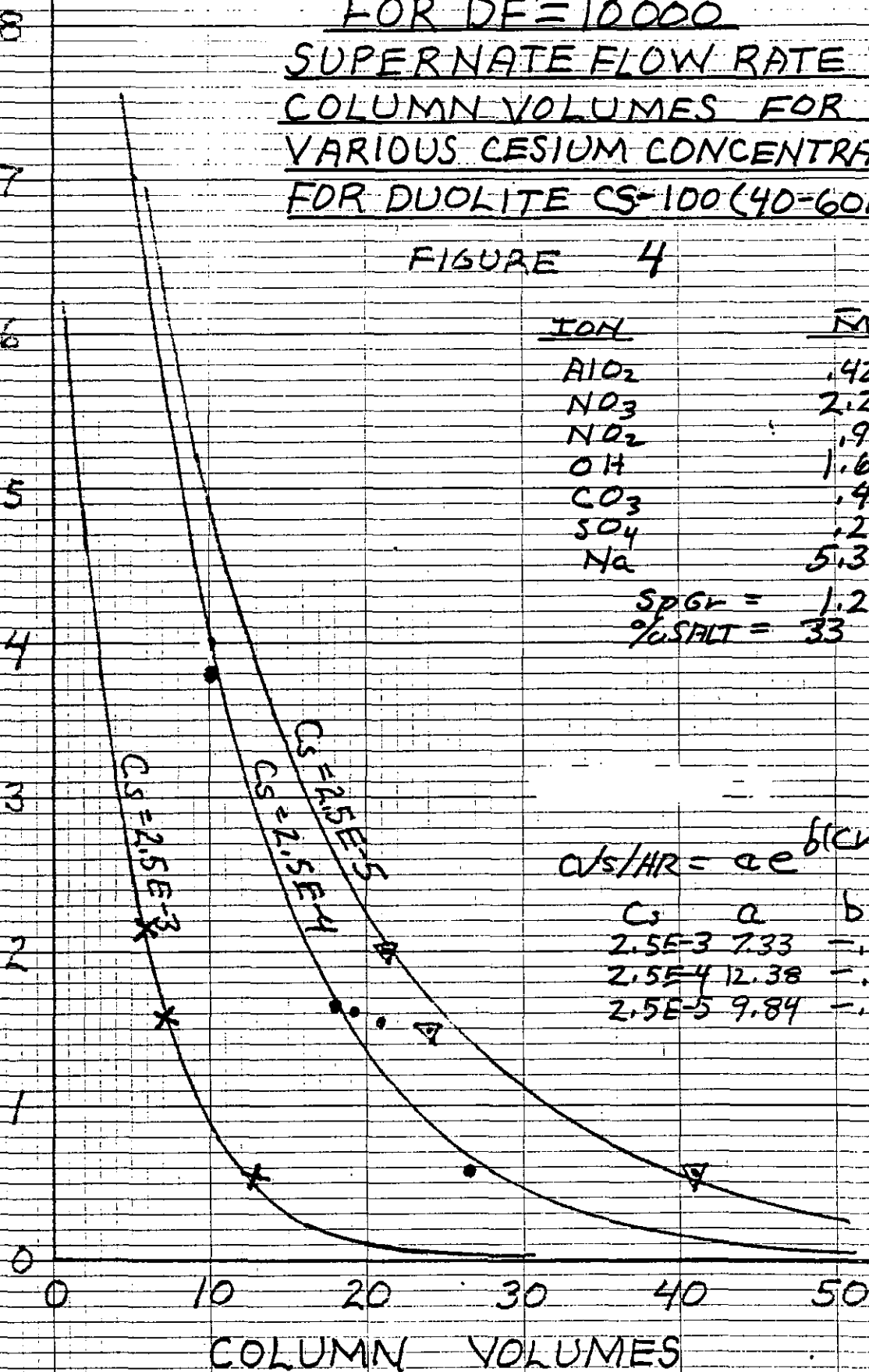
COLUMN VOLUMES / HOUR + CV'S / HR

ION	M
AlO ₂	.423
NO ₃	2.2
NO ₂	.95
OH	1.62
CO ₃	.48
SO ₄	.24
Na	5.3

Sp Gr = 1.29
 % SALT = 33

$$CV'S/HR = ae^{b(CV'S)}$$

C	a	b
2.5E-3	7.33	-.0732
2.5E-4	12.38	-.1000
2.5E-5	9.84	-.0732

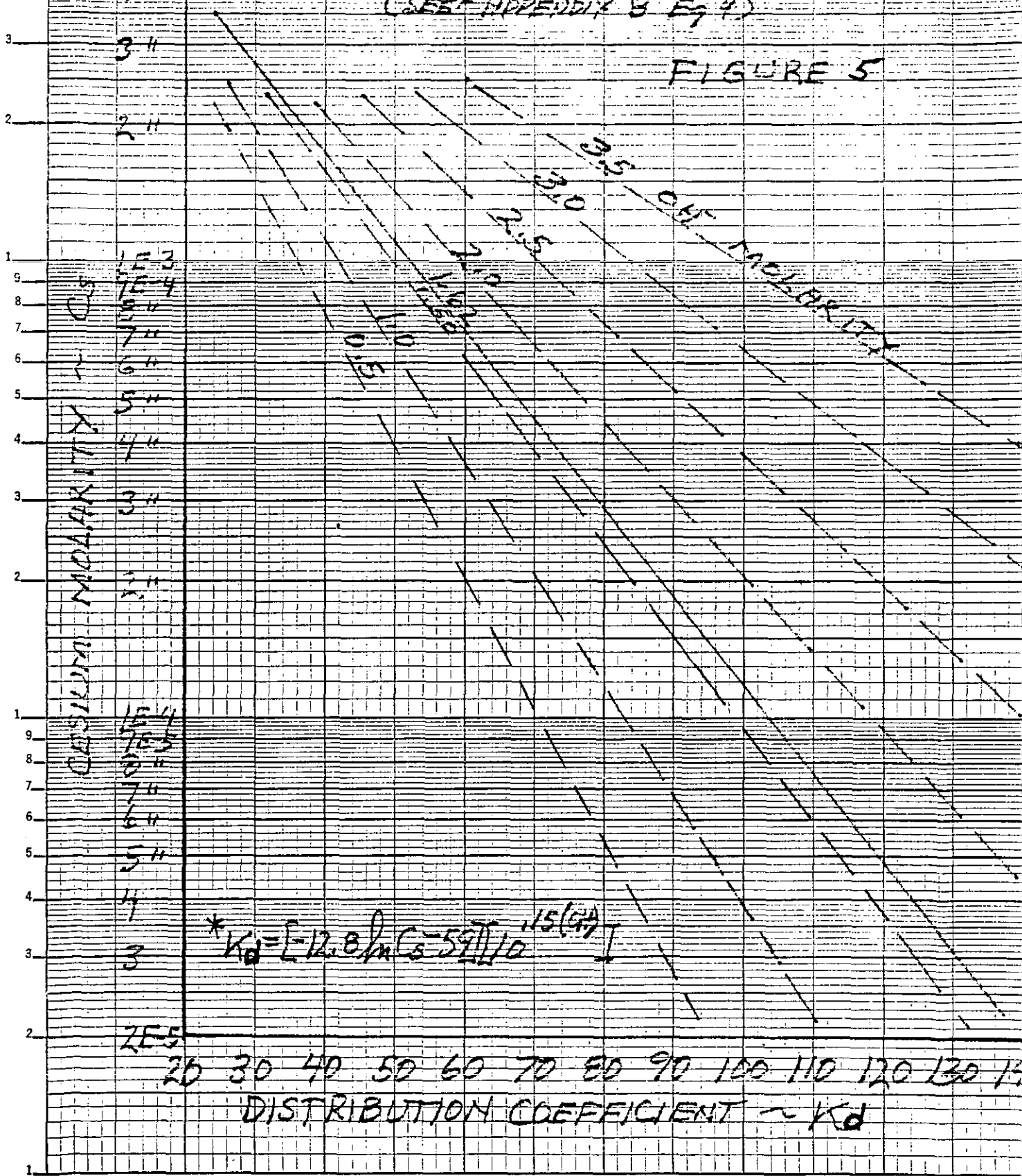


COLUMN VOLUMES

DISTRIBUTION COEFFICIENT (K_d)
FOR DIOLITE CS-100
VS CESIUM CONCENTRATION
IN SUPERNATE

EXTRAPOLATED TO OTHER OH⁻ CONCENTRATIONS
(SEE APPENDIX B Eq 4)

FIGURE 5



APPENDIX A

Experimental data plots are shown in the following figures.

The reasoning for plotting the experimental data is shown in Figure 6. The data plots are shown in Figures 7 to 18. A tabulation of the experiments run is shown in Table III.

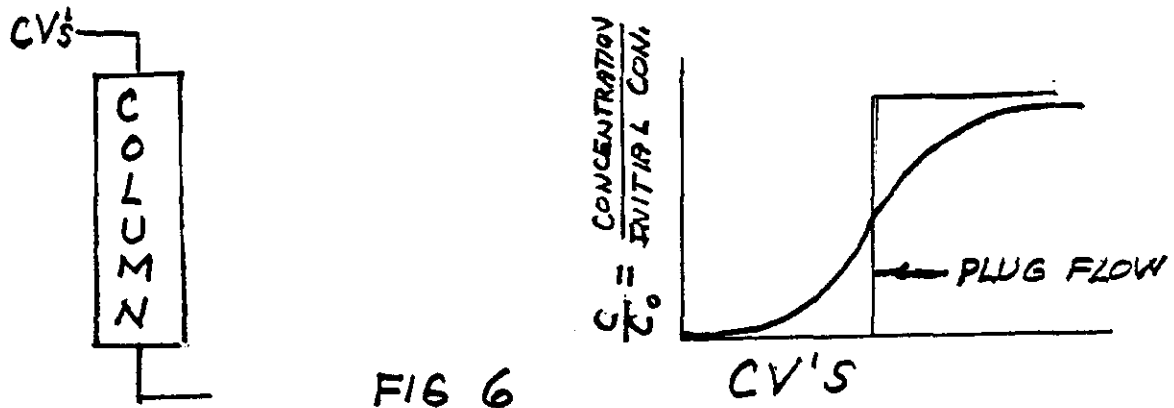
EXPERIMENTAL NOMENCLATURE

FIG 6

$$CV's = \frac{V}{V_c} = K_d [\rho(1-\phi)] + \phi = K_d \rho_B + \phi$$

ϕ = volume fraction, liquid/bed volume

ρ = density resin wet

CV = volume of column

CV's = volume of feed

$\rho(1-\phi)$ = bulk density of resin wet

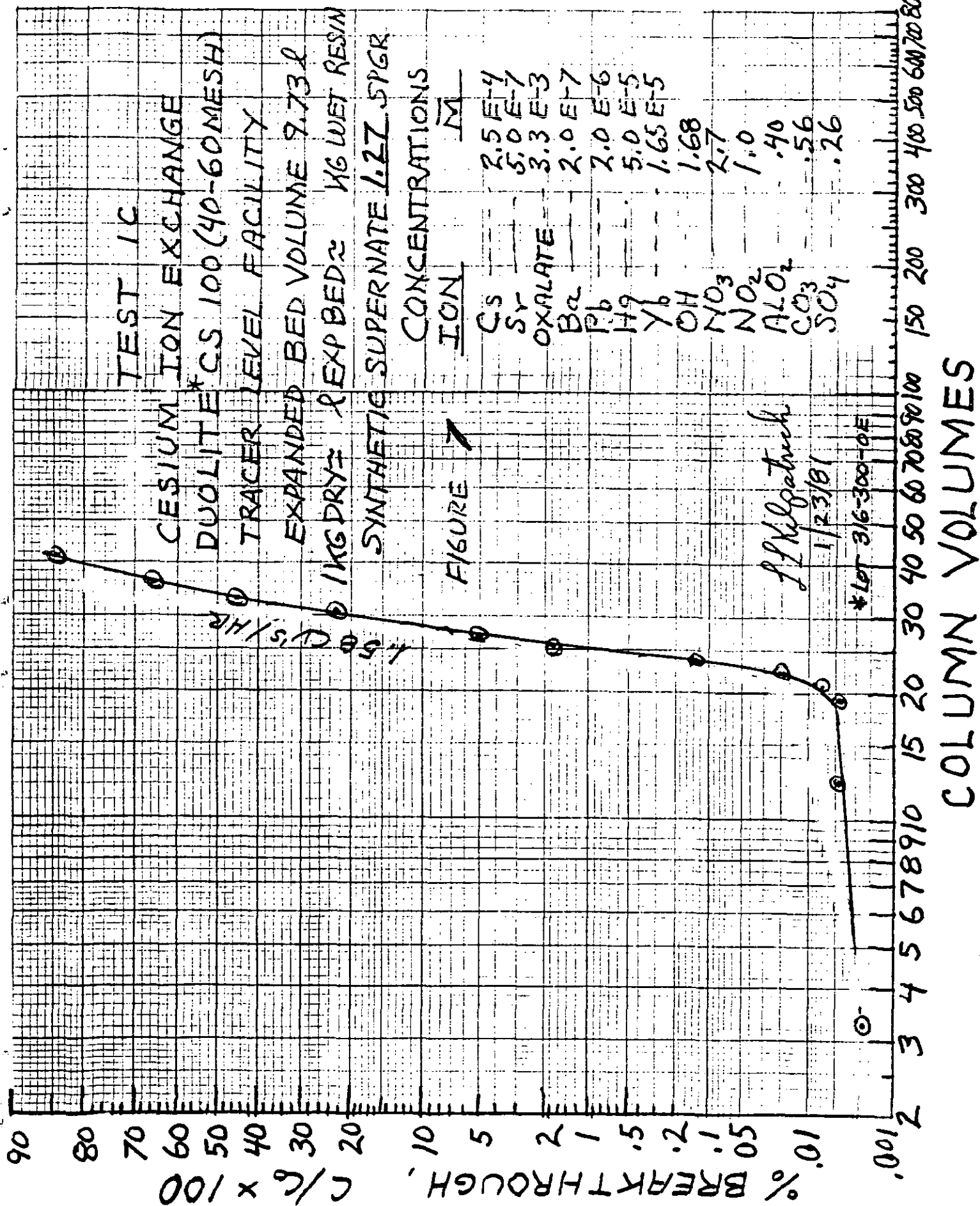
let ρ_B = bulk density = $\frac{\text{wt dried form}}{\text{volume in liquid}}$

$$K_d = q/\underline{c} = \frac{\text{volume bed}}{\text{volume feed}}$$

q = solid concentration, gm equal/ml bed volume

\underline{c} = liquid concentration, (g-equiv)/ml

In Practice: $\rho_B K_d \approx 1.1$ [(CV)'s at 60% breakthrough]



CONCENTRATION IN SUPERNATE
Σ% AND % C_s

100
90
80
70
60
50
40
30
20
10
0

COLUMN VOLUMES

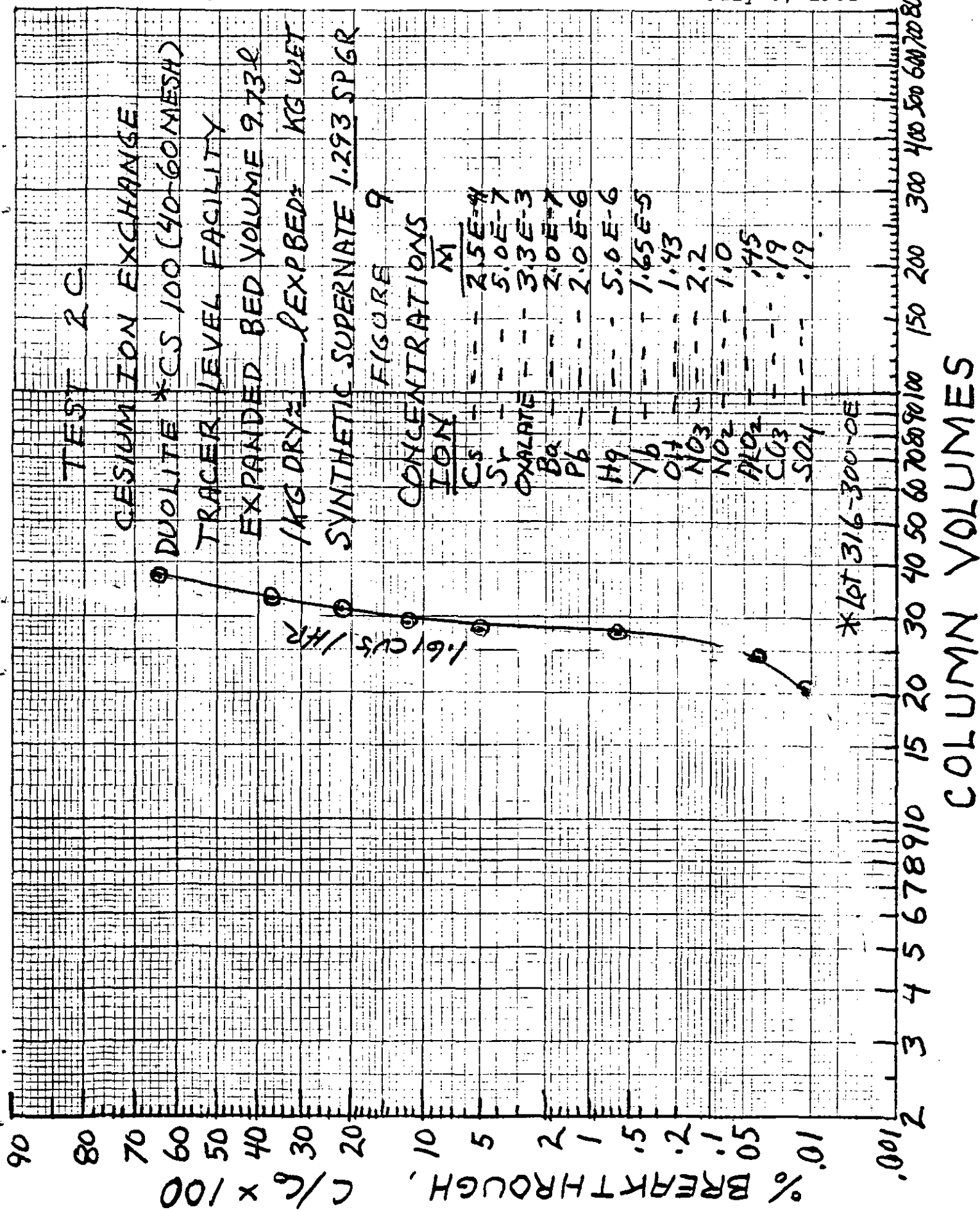
TEST 1C
ELUTION CYCLE
TRACER LEVEL FACILITY

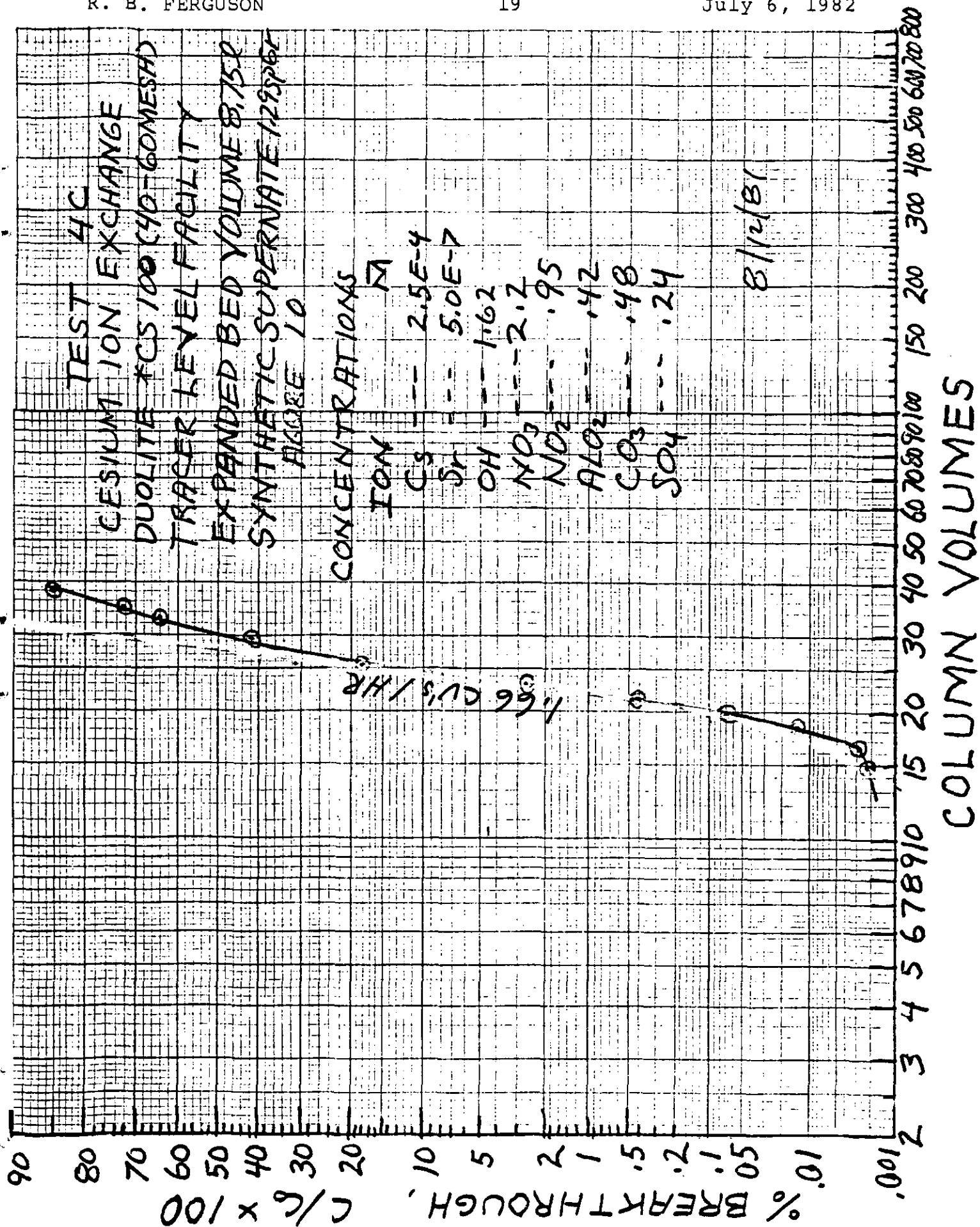
8

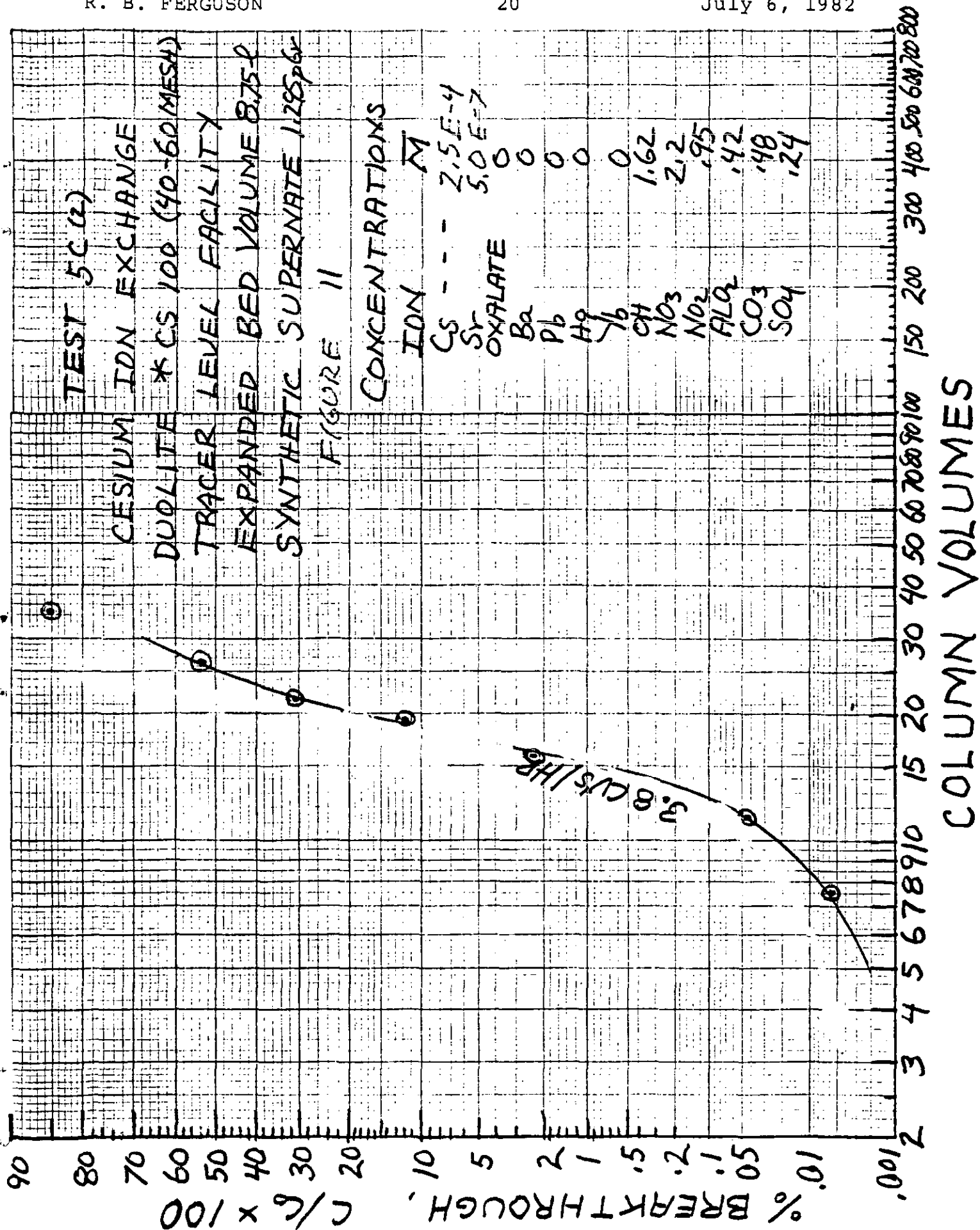
Σ%	CV's
100	6.0
99.5	4.5
99.0	4.2
95.0	3.6

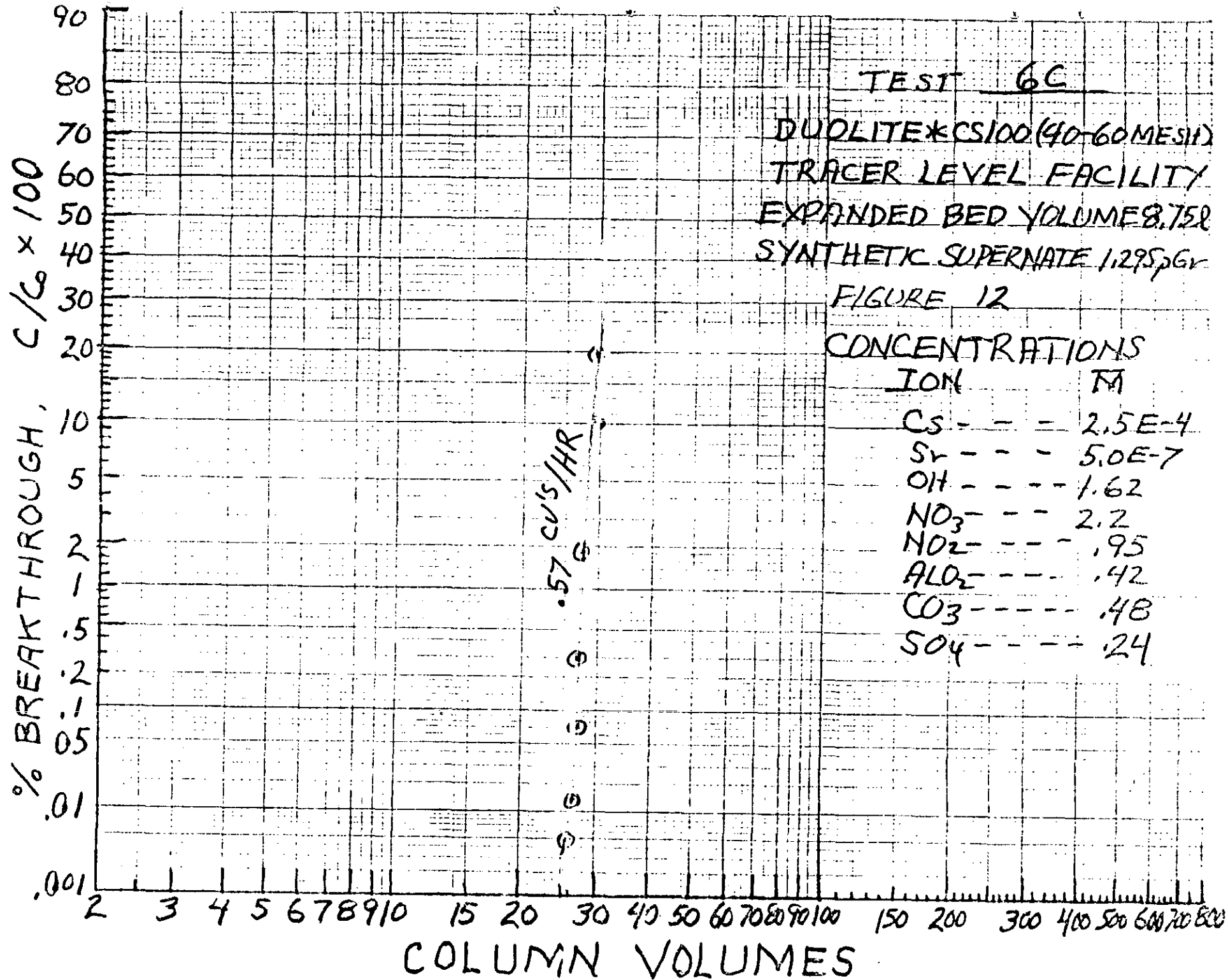
Σ%

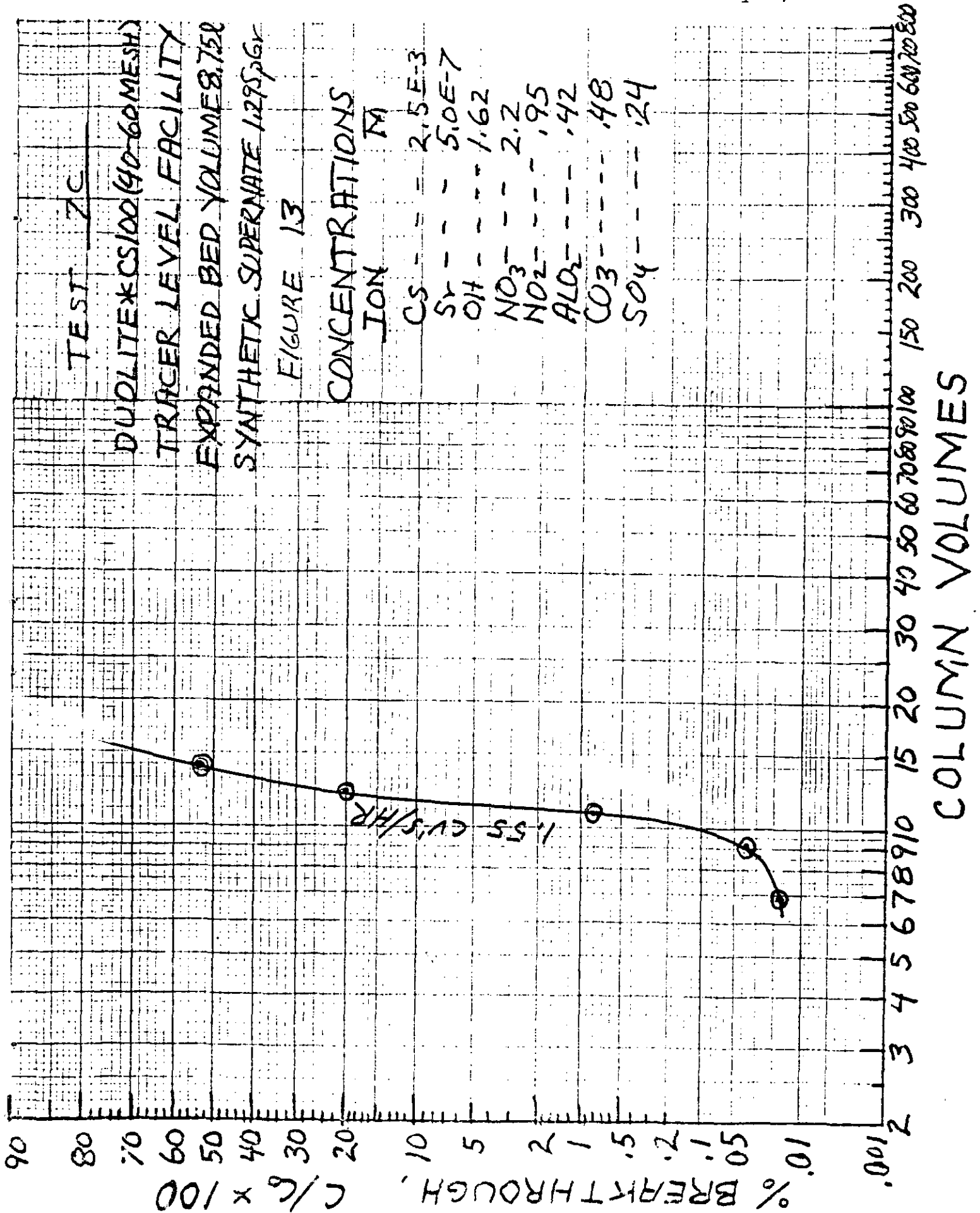
%

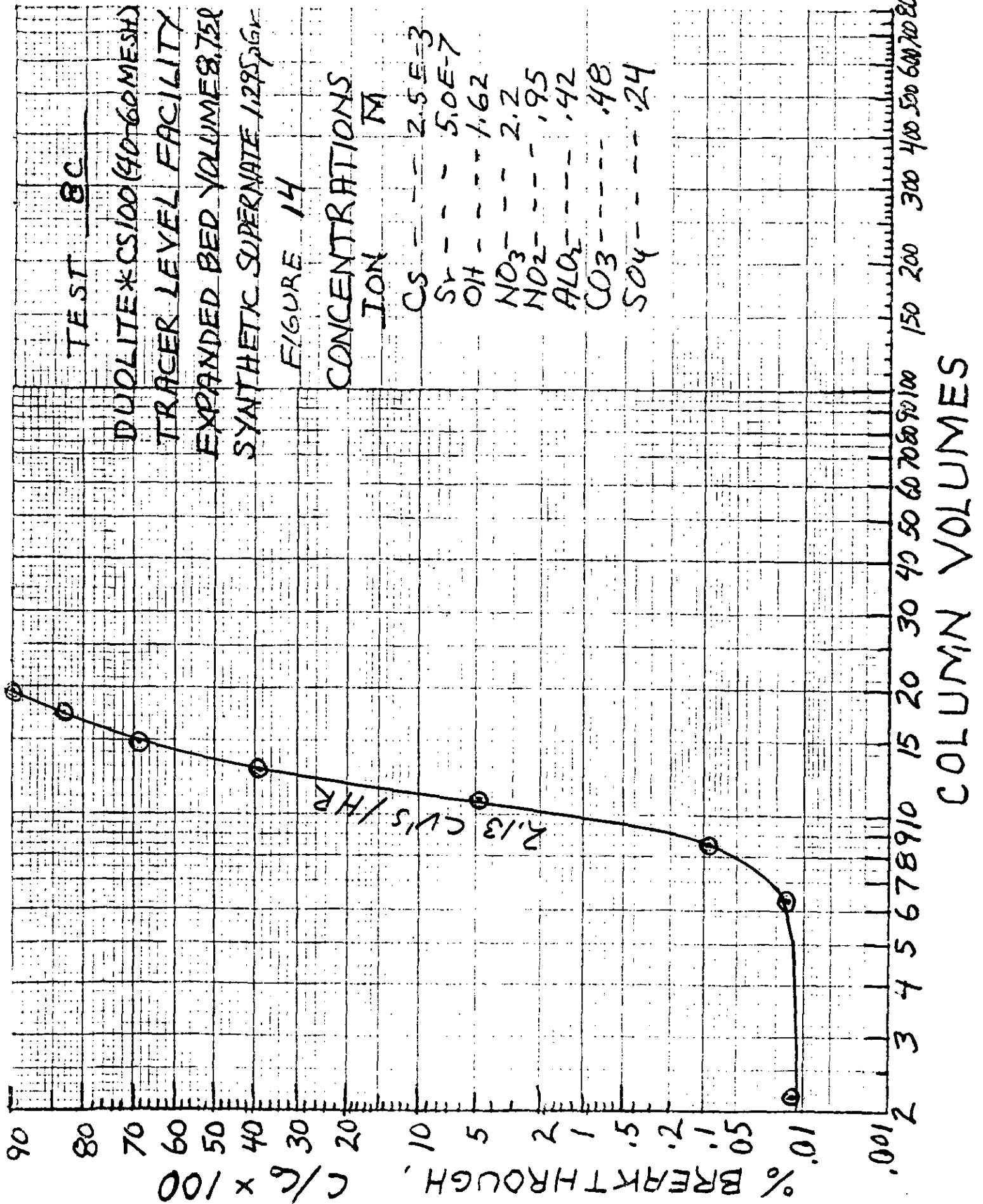












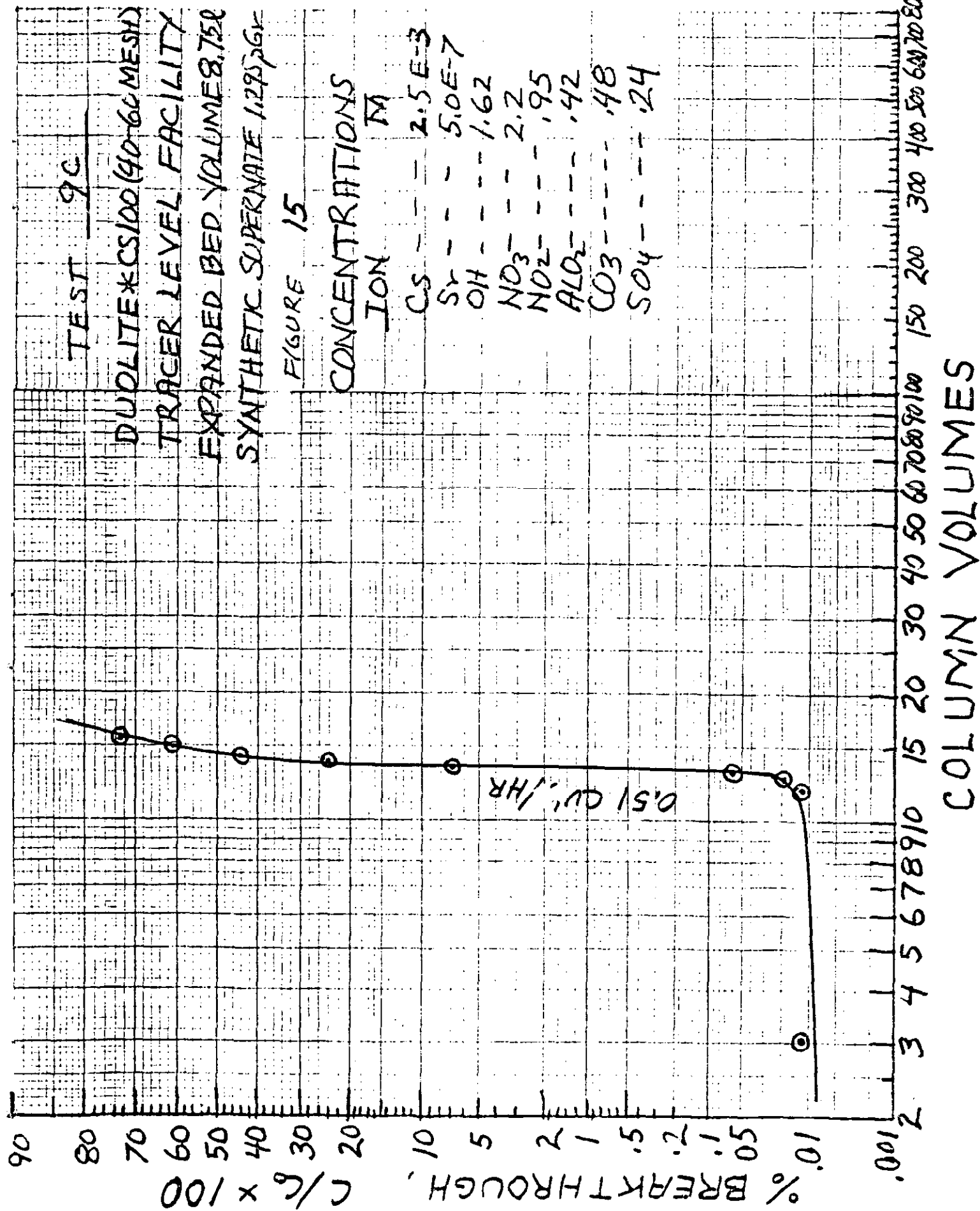
DUOLITE*CS100 (40-60 MESH)
TRACER LEVEL FACILITY
EXPANDED BED VOLUME 8.75L
SYNTHETIC SUPERNATE 1.295 g/L

FIGURE 15

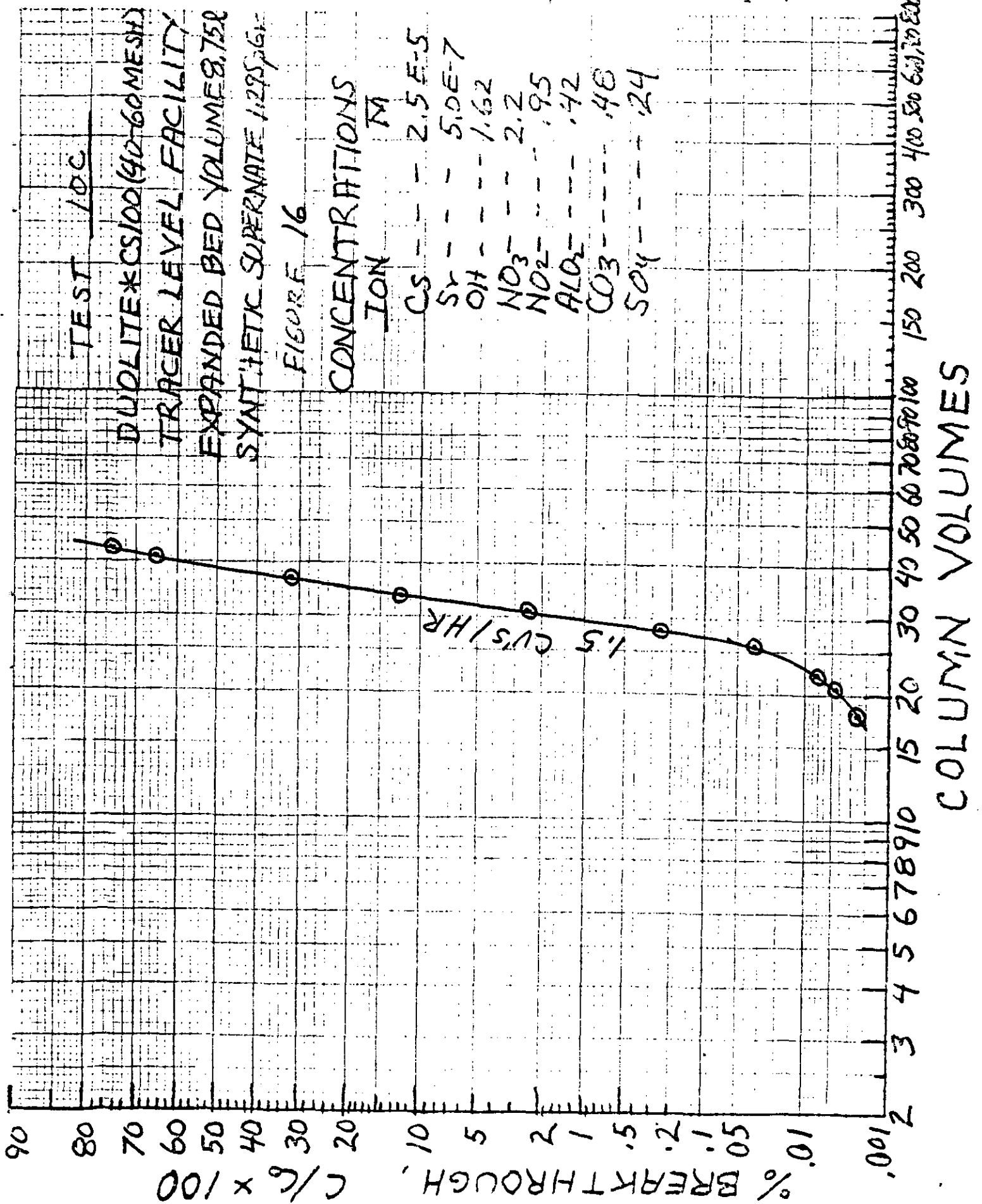
CONCENTRATIONS

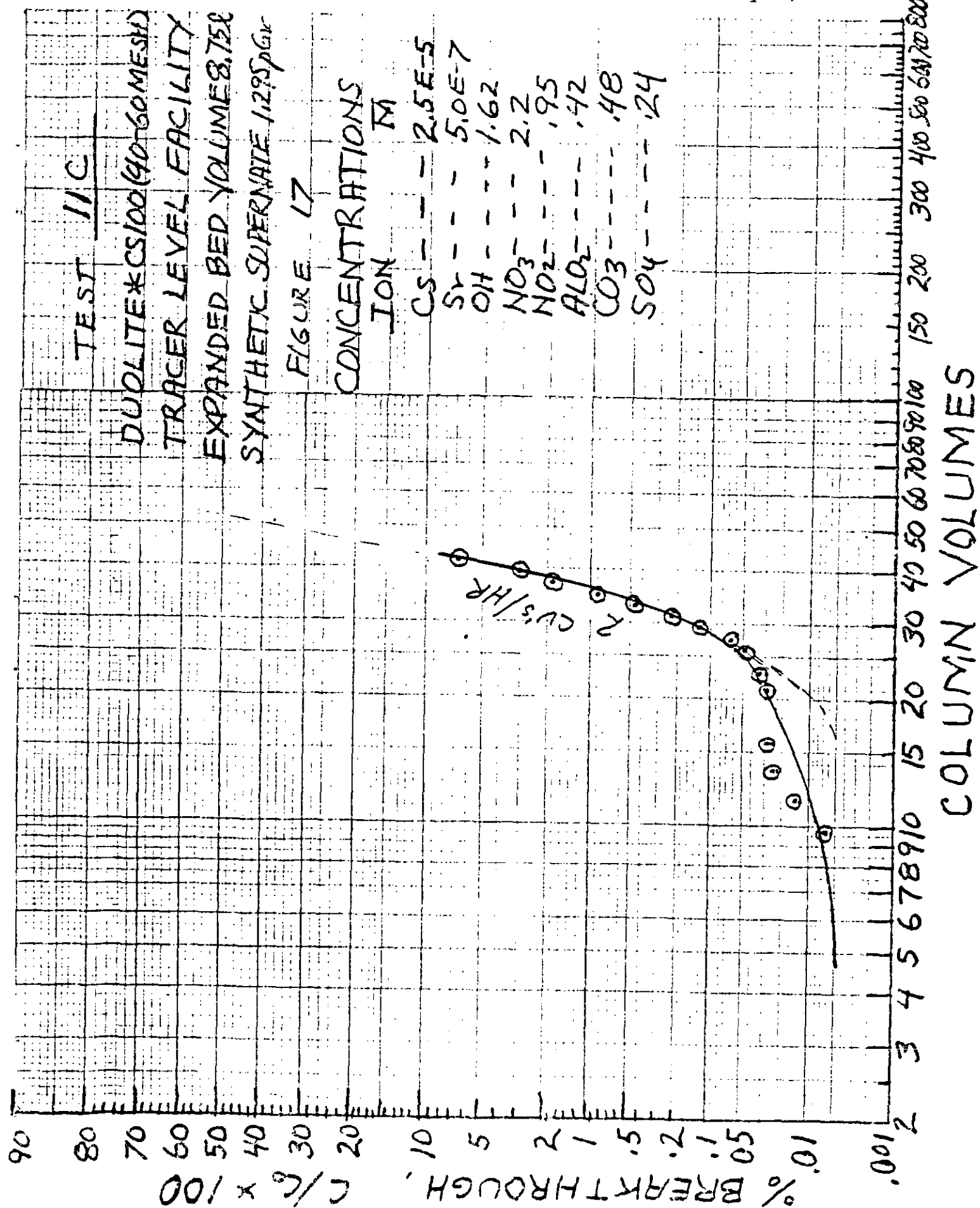
ION FM

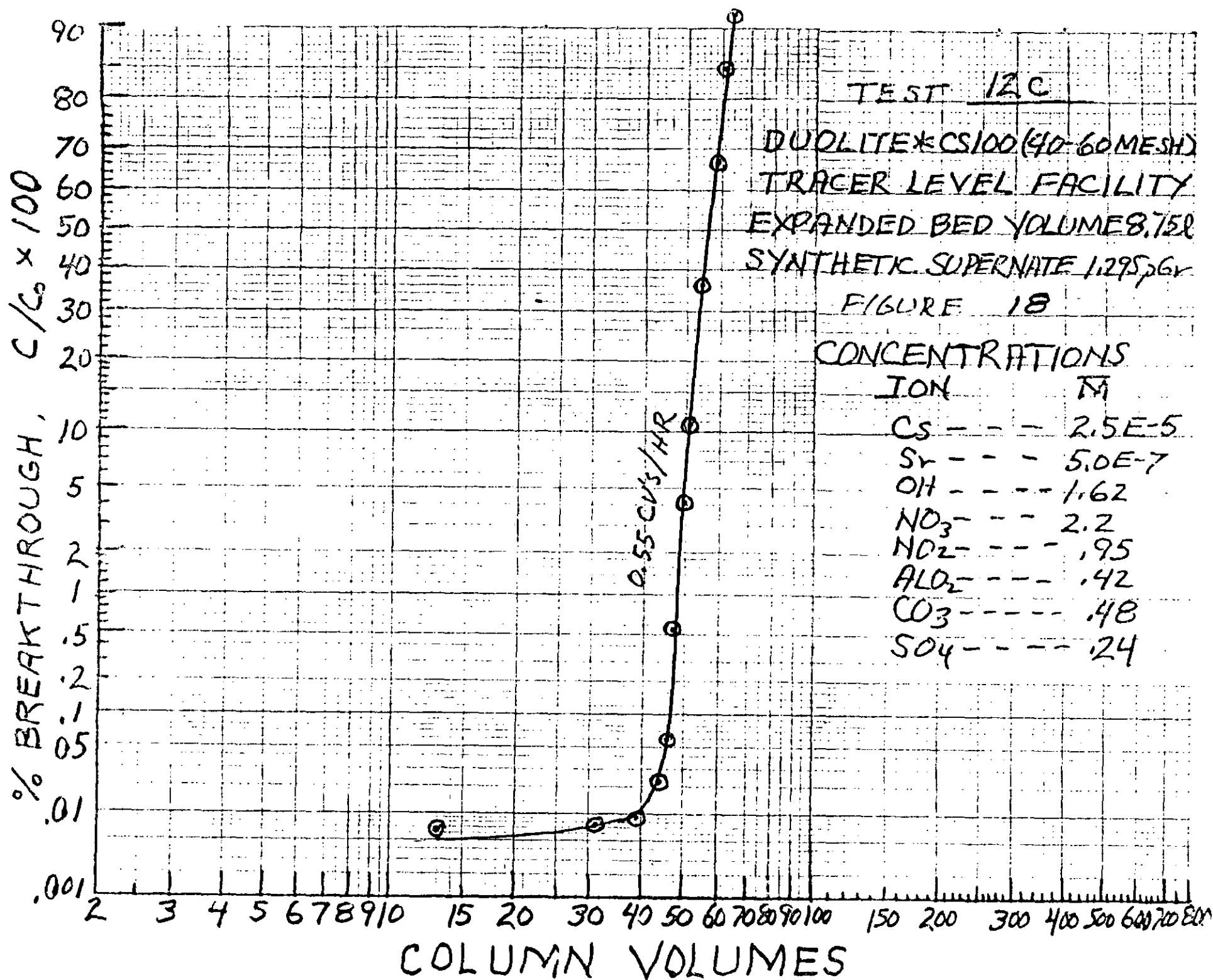
CS --- 2.5E-3
Sr --- 5.0E-7
OH --- 1.62
NO₃ --- 2.2
NO₂ --- .95
AL(OH)₃ --- .42
CO₃ --- .48
SO₄ --- .24



COLUMN VOLUMES







APPENDIX B

Data relating the effect of cesium and hydroxyl concentration on the K_d of Duolite CS-100 was measured by Eber⁴ and is shown on Table VII. This data was fit to the following equation:

$$\log K'_d = \left[\frac{.805 \log Cs + .263}{.161 \log Cs - 1} + (.15)(\overline{OH}) \right] \quad (1)$$

The K_d values measured in the Tracer Level Facility (Table IV and Figure 3) were fit to the following equation:

$$K_{d \text{ obs}} = (-22.45 \ln(Cs)) - 103 \quad (2)$$

The following equations were used to predict the K_d value at other cesium and hydroxide conditions:

$$K_{d \text{ new}} = [K_{d \text{ obs}}] \left[\frac{K'_{d \text{ new}}}{K'_{d \text{ cal}}} \right] \quad (3)$$

Substituting 1 and 2 in 3, gives:

$$K_{d \text{ new}} = - [12.83 \ln(Cs) + 58.9] [10^{(.15)(\overline{OH})}] \quad (4)$$

which was used to plot Figure 5.

A general case equation for extrapolating from any observed K_d to a K_d at any new cesium or hydroxyl level was developed from equations 1 and 3.

$K_{d_{\text{new}}}$ = predicted value of K_d based on new Cs & OH

$K_{d_{\text{obs}}}$ = observed K_d at Cs and OH given

Cs_{new} = Cs molarity at predicted K_d

OH_{new} = hydroxide molarity at predicted K_d

Cs_{obs} = cesium molarity at observed K_d

OH_{obs} = hydroxide molarity at observed K_d

$$K_{d_{\text{new}}} = \left[(K_{d_{\text{obs}}}) \right] \left[\frac{10^{\left[\frac{.805 \log Cs_{\text{new}} + .263}{.161 \log Cs_{\text{new}} - 1} + .15 \overline{OH}_{\text{new}} \right]}}{10^{\left[\frac{.805 \log Cs + .263}{.161 \log Cs - 1} + .15 \overline{OH}_{\text{obs}} \right]}} \right] \quad (5)$$

TABLE V
(Ref 4)

K_d' for Duolite CS-100 at Various \overline{Cs} and \overline{OH} Concentrations and
6M Total Sodium

OH^-	$C_{orig.}$	C_{eq}	$(K_d')^*$
4M	1×10^{-1}	8.49×10^{-2}	13.3
"	1×10^{-2}	6.00×10^{-3}	49.8
"	1×10^{-3}	3.59×10^{-4}	134
"	1×10^{-4}	2.94×10^{-5}	179
"	1×10^{-5}	1.16×10^{-6}	568
2M	1×10^{-1}	8.89×10^{-2}	9.37
"	1×10^{-2}	6.83×10^{-3}	34.4
"	1×10^{-3}	4.92×10^{-4}	77.1
"	1×10^{-4}	2.57×10^{-5}	216
"	1×10^{-5}	1.33×10^{-6}	486
1M	1×10^{-1}	9.53×10^{-2}	3.72
"	1×10^{-2}	8.02×10^{-3}	18.5
"	1×10^{-3}	5.54×10^{-4}	60.1
"	1×10^{-4}	3.39×10^{-5}	146
"	1×10^{-5}	1.94×10^{-6}	312
"	1×10^{-6}	1.32×10^{-7}	492
"	1×10^{-7}	1.04×10^{-8}	643
0.1M	1×10^{-1}	9.62×10^{-2}	3.00
"	1×10^{-2}	8.56×10^{-3}	12.5
"	1×10^{-3}	6.66×10^{-4}	37.5
"	1×10^{-4}	4.88×10^{-5}	78.4
"	1×10^{-5}	3.48×10^{-6}	140
"	1×10^{-6}	3.16×10^{-7}	500

*

Based on bulk density = .413 = ρ_B

$$\rho_B = \frac{\text{wt of oven dried Na form}}{\text{vol of Na form in 1M NaOH}}$$

APPENDIX C

TABLE VI

3

Chemical & Physical Properties of Duolite CS-100PropertyWeight Ratios

R_1	air dried H^+ form/wet H^+ form ⁽¹⁾	0.681
R_2	wet Na^+ form/wet H^+ form ⁽¹⁾	1.502
R_3	dry Na^+ form/wet H^+ form ⁽¹⁾	0.911
R_4	oven dried H^+ form/air dried H^+ form	1.09

Bulk Densities, g/ml

B_H	H^+ form ⁽²⁾	0.694
B_{Na}	Na^+ form ⁽³⁾	0.515
ρ_B	Na^+ form ⁽⁴⁾	0.413

Capacity

$C(g)$	meq/g ⁽⁵⁾	3.65
$C(V)$	meq/ml ⁽⁶⁾	1.71
Lot No. of resin		316-300-0E

(1) H^+ form as received from vendor.

(2) Weight of wet H^+ form ⁽¹⁾/volume of H^+ form in water.

(3) Weight of wet H^+ form ⁽¹⁾/volume of Na^+ form in 1M NaOH.

(4) Weight of oven dried Na form/volume of Na^+ form in 1M NaOH.

(5) Meq/g of dry Na^+ form.

(6) Meq/ml of Na^+ form in 1M NaOH.

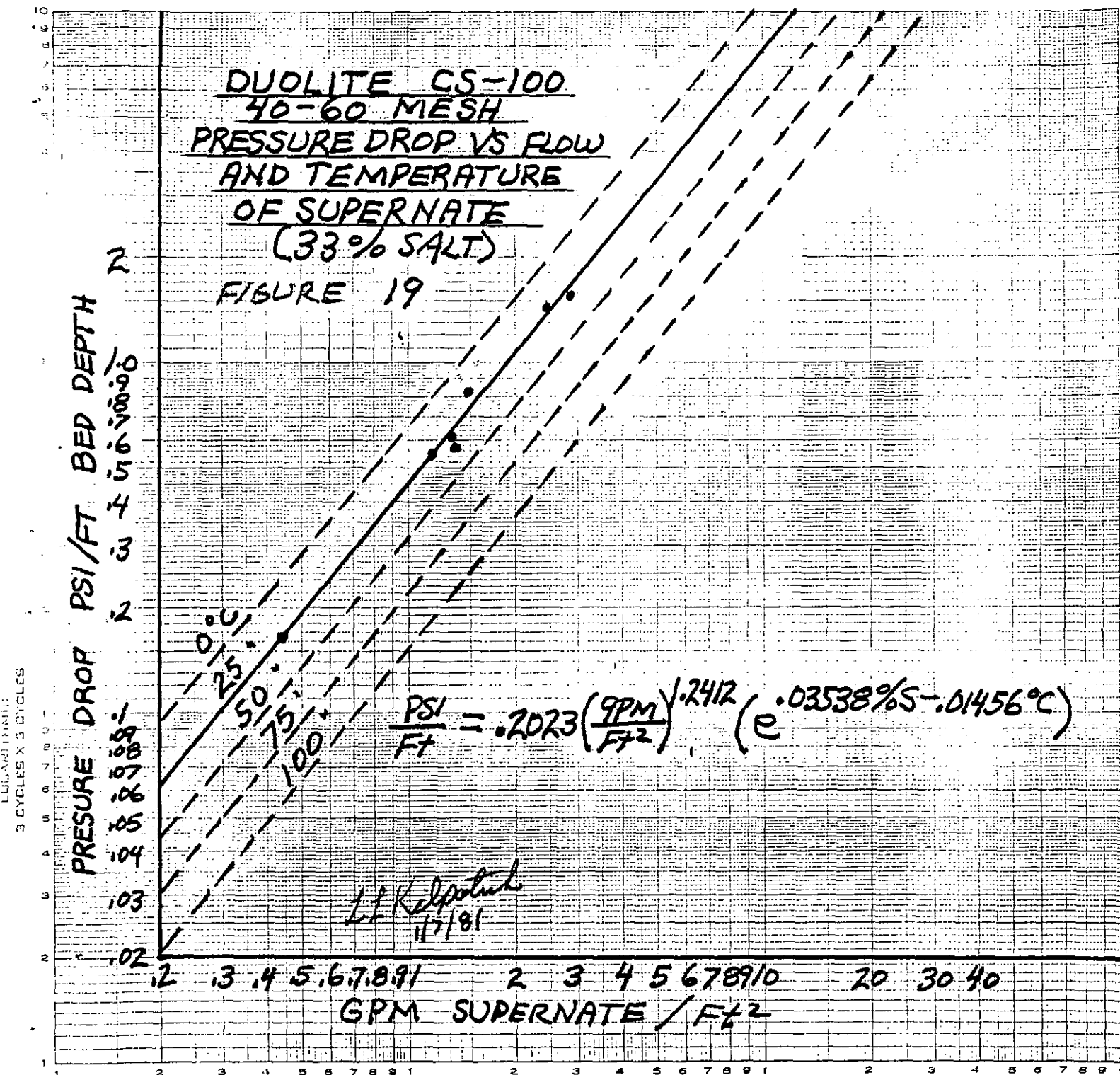


TABLE VII

Pressure Drop vs Flow Rate of Supernate (33% Salt) at 25°C
(Load Cycle - 3" Diameter Column)

$$\text{psi/ft} = .4518 \left[\frac{\text{gpm}}{\text{ft}^2} \right]^{1.2412}$$

<u>Test No.</u>	<u>Pressure Drop lb/in²</u>	<u>Height Column Inches</u>	<u>Flow Rate</u>		<u>psi/ft</u>
			<u>CV's/hr</u>	<u>gpm/ft²</u>	
4C	3.67	77.5	1.65	1.33	.568
	3.96	76.5	1.65	1.31	.621
5C(2)	9.4	72.0	3.8	2.85	1.567
6C	1.0	74.	0.57	.439	.162
10C	3.3	73.	1.5	1.14	.542
11C	5.1	74	1.9	1.46	.827
X	9.6	81.3	2.87	2.42	1.42

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