



ANALYTICAL METHOD

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Supersedes: LAD-AR 89.06

DOWM 100718-LE90A

Low Percent Levels of Inert Gases in Chlorine

1. Scope

This method outlines the use of an automated gas chromatographic system to determine the percent levels of hydrogen, oxygen, nitrogen, carbon dioxide, and carbon monoxide in chlorine.

2. Principle

A gaseous chlorine sample is introduced onto a series of three gas chromatographic columns. The first column allows the inert gases to **elute** while selectively trapping the chlorine, which is later removed by **backflushing** the column. The **inerts** then pass through a second column where hydrogen, oxygen, and nitrogen pass through unresolved, and carbon monoxide and carbon dioxide are completely separated. The hydrogen, oxygen, and nitrogen then enter a third column where they are fully resolved. As the carbon monoxide enters the third column, that column is isolated from the system, and the carbon dioxide is allowed to **elute** directly from the second column into the detector. The third column is then switched back into series with the other two columns, and the carbon monoxide is **eluted**. (See Figure 1)

3. Safety

- 3.1 Chlorine is a highly toxic and corrosive substance, and it should be handled with extreme care. Consult the Material Safety Data Sheet for chlorine before handling this substance.
- 3.2 Liquid samples taken in cylinders should have dip legs installed to allow only 85% filling of the cylinders. This will serve to prevent cylinder rupture, since pressure relief devices would be undesirable.
- 3.3 Vent the gas sampling system to a Class A fume hood after scrubbing through a minimum of a 7% sodium hydroxide solution.

- 3.4 Sodium hydroxide is a strong alkali and is dangerous when improperly handled. **Monogoggles** and gloves must be worn by personnel handling sodium hydroxide.
- 3.5 Each analyst should be acquainted with potential hazards of the reagents, products, and solvents before beginning laboratory work. SOURCES OF INFORMATION INCLUDE: MATERIAL SAFETY DATA SHEETS, LITERATURE AND OTHER RELATED DATA. Safety information of non-Dow products should be requested from the supplier. Disposal of reagents, reactants, and solvents must be in compliance with local, state, and federal laws and regulations.

4. Interferences

Care must be taken not to contaminate the samples and/or standards with air, as this would yield erroneous results. If results are suspect based on the analytical history of the product, the data should be confirmed by an alternate method.

5. Apparatus and Reagents

- 5.1 1/16 in. eight-port switching valve (valve **B**) with an automated air actuator from **Valco** Instruments Co., Houston, Texas 77024
- 5.2 1/16 in. **Hastelloy C** ten-port switching valve (Valve A) with an automated air actuator from **Valco** Instruments Co., Houston, Texas 77024
- 5.3 Sample Loop - one (1) mL - 1/8 in. Nickel
- 5.4 Hewlett-Packard 5890A Gas **Chromatograph** with a thermal conductivity detector, valve compartment, and valve switching control available from Hewlett-Packard Corp., Route 41, Avondale, PA 19311
- 5.5 Hewlett-Packard 3396A Integrator available from Hewlett-Packard Corp., Route 41, Avondale, PA 19311
- 5.6 **Restrictor** - 1/16 in. **Nupro micrometering** valve with **Swagelok** fittings from Capital Valve and Fitting Co., Inc., Baton Rouge, Louisiana 70809
- 5.7 Stripper Column- 20 in. x 1/8 in. Nickel 200 tubing packed with **PorapakS** 80/100 mesh available from **Teklab** Inc., 9138 Mammoth Drive, Baton Rouge, LA 70814
- 5.8 Analytical Column - 20 ft x 1/8 in. 304 stainless steel tubing packed with **Hayesep N** 80/100 mesh available from **Teklab** Inc., 9138 Mammoth Drive, Baton Rouge, LA 70814

- 5.9 Mole Sieve - 6 ft x 1/8 in. 304 stainless steel tubing packed with Molecular Sieve 5A 80/100 mesh available from Teklab Inc., 9138 Mammoth Drive, Baton Rouge, LA 70814
- 5.10 Argon, analytical grade carrier gas is available from Mon-Arc Specialty Gases, Baton Rouge, LA.

6. Chromatographic conditions

A copy of the integration method used for the PERCENT analyses on the Hewlett-Packard 3396A Integrator is shown in Figure 2.

6.1 Temperature

- 6.1.1 Oven temperature 90°C (isothermal)
- 6.1.2 Injection port A 100°C
- 6.1.3 Detector 150°C

6.2 Carrier Gas Flows (Argon)

- 6.2.1 Flow A - 20 cm³/minute
- 6.2.2 Flow 1 - 30 cm³/minute
- 6.2.3 Aux. Flow - 30 cm³/minute
- 6.2.4 Flow 2 - approx. 5 cm³/minute. This flow may need to be adjusted slightly to allow proper elution of the carbon monoxide peak.

6.3 Sample Size: 1 mL

6.4 Valve Timing

- 6.4.1 Valve A On - 0.00 min Off - 1.50 min
- 6.4.2 Valve B timing is different for each Molecular Sieve column, but approximate values are as follows:

On - 7.40 min Off - 11.50 min

6.5 Approximate Retention Times (See Figure 3)

- 6.5.1 Hydrogen 5.0 minutes
- 6.5.2 Oxygen 6.2 minutes
- 6.5.3 Nitrogen 6.9 minutes
- 6.5.4 Carbon Dioxide 11.0 minutes
- 6.5.5 Carbon Monoxide 13.4 minutes

7. Calibration

- 7.1 Run Argon blanks before attempting to calibrate, because air leaks in the chromatographic system will be revealed by this procedure.
- 7.2 In order to achieve the highest accuracy, the level of **inerts** in the gas standards should be as near as possible to the actual level **inerts** expected in the sample. Standards should be run at least three times prior to a **recalibration**, and the calibration should be checked daily.
- 7.3 Actual chlorine samples should be analyzed in triplicate, and the average value of the three runs should be used as the measured level.

8. Procedure

- 8.1 Attach the sample cylinder to the gas sample line and pulse purge the line 5 or 6 times by opening and closing the cylinder valve quickly.
- 8.2 Slowly purge the sample line at a moderate rate for 20 - 30 seconds. The purge should flow through the sample loop into a Class A fume hood with a scrubber containing at least a 7% sodium hydroxide solution.
- 8.3 Close the cylinder valve finger-tight.
- 8.4 Allow the sample to equilibrate to **atmospheri** pressure by observing the cessation of sample bubbling in the fume hood.
- 8.5 Start the gas chromatographic run on the Hewlett-Packard 3396A integrator.
- 8.6 From this point, the entire analysis is automated by using electronically controlled air actuators to turn two separate gas switching valves. The following text is a description of the automated steps that are occurring in the instrument. (See Figures 4 - 8).
 - 8.6.1 Figure 4 shows the **valving** in the OFF position, prior to the start of the run. The sample is being purged through the sample loop, the stripper column is being **backflushed** to Vent **#1**, the mole sieve column is in line with the detector, and the **restrictor** valve is going to Vent **#2**. The **restrictor** valve has been set to match the restriction caused by the mole sieve column as to minimize the flow surge when the valve is switched.
 - 8.6.2 Figure 5 shows the **valving** positions that occur when the run is started. Valve A switches into the ON position and injects the sample in the

sample loop onto the stripper column. The inert gases then move from the stripper column onto the analytical column.

- 8.6.3 After all of the inert gases have passed from the stripper column onto the analytical column, Valve A is then switched back into the OFF position so that the chlorine can be **backflushed** from the stripper column. (See Figure 6).
- 8.6.4 After the Nitrogen peak **elutes**, Valve **B** is switched into the ON position before the carbon dioxide peak **elutes** from the analytical column. The mole sieve column is isolated, and the **restrictor** valve is placed in-line to let the carbon dioxide pass straight from the analytical column to the detector when it **elutes**. (See Figure 7)
- 8.6.5 After the carbon dioxide peak **elutes**, valve **B** is switched back into the OFF position, and the, carbon monoxide peak is allowed to **elute** from the mole sieve. (See Figure 8).
- 8.6.6 The integration stops the run according to the stop time set in the run timetable, and the report prints out automatically. As soon as the report is printed, the gas **chromatograph** is ready for another run.

9. Precision

Data obtained by this procedure shows precision as follows

Components	Concentration**	Relative Std. Dev.	Relative Precision***
H ₂	0.041%	1.2%	2.4%
O ₂	1.91%	1.2%	2.4%
N ₂	1.69%	0.6%	1.2%
CO ₂	3.65%	1.2%	2.4%
CO*	0.500%	2.4%	4.8%

* Results for CO are from % Recovery Study using a standard gas mixture, because the chlorine sample analyzed did not contain CO.

** Concentration at which precision was determined.

*** Relative precision at the 95% confidence level

10. Accuracy

Analysis of a series of **synthetic** mixtures gave recoveries as follows:

Components	Concentration	% Recovery	Relative Std. Dev.
H ₂	0.251%	100%	0.4%
O ₂	0.997%	101%	0.8%
N ₂	4.02%	100%	0.3%
CO ₂	0.500%	99%	5.0%
CO	0.500%	100%	2.4%

11. Linearity

Linearity of the Thermal Conductivity Detector's response was confirmed over a concentration range of 0.1 - 1.0 for H₂ 0.5 - 3.0 % for O₂ 1.0 - 4.0 for N₂ 0.25 - 2.0 % for CO₂, and 0.25 - 2.0 % for CO

12. Limit of Detection

The method detection limit was found to be 0.01% for H₂ 0.05% for O₂ 0.03% for N₂ 0.1% for CO₂, and 0.1% for CO.

13. Notes

- 13.1 By substituting an eight-port valve for the six-port valve used in Analytical Method No. 76.07 a constant helium flow could be kept on the mole sieve column, even when it was switched out-of-line. This valving change prevented oxygen infusion onto the mole sieve column, which had been a problem when the column was deadened using a six-port valve.
- 13.2 Nickel 200 tubing should be used on any surface that could possibly contact with the Chlorine, as this will eliminate some reactivity problems that occurred when stainless steel tubing was used. For best efficiency, the sample in and out lines should be replaced about every 6 - 9 months.

- 13.3 Hayesep N porous polymer was used instead of Porapak N because of the overall higher quality of the polymer, and thus enhanced separating power.

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FIGURE 1: PRINCIPLE OF ANALYSIS

PPM LEVEL ANALYSIS PERCENT LEVEL ANALYSIS

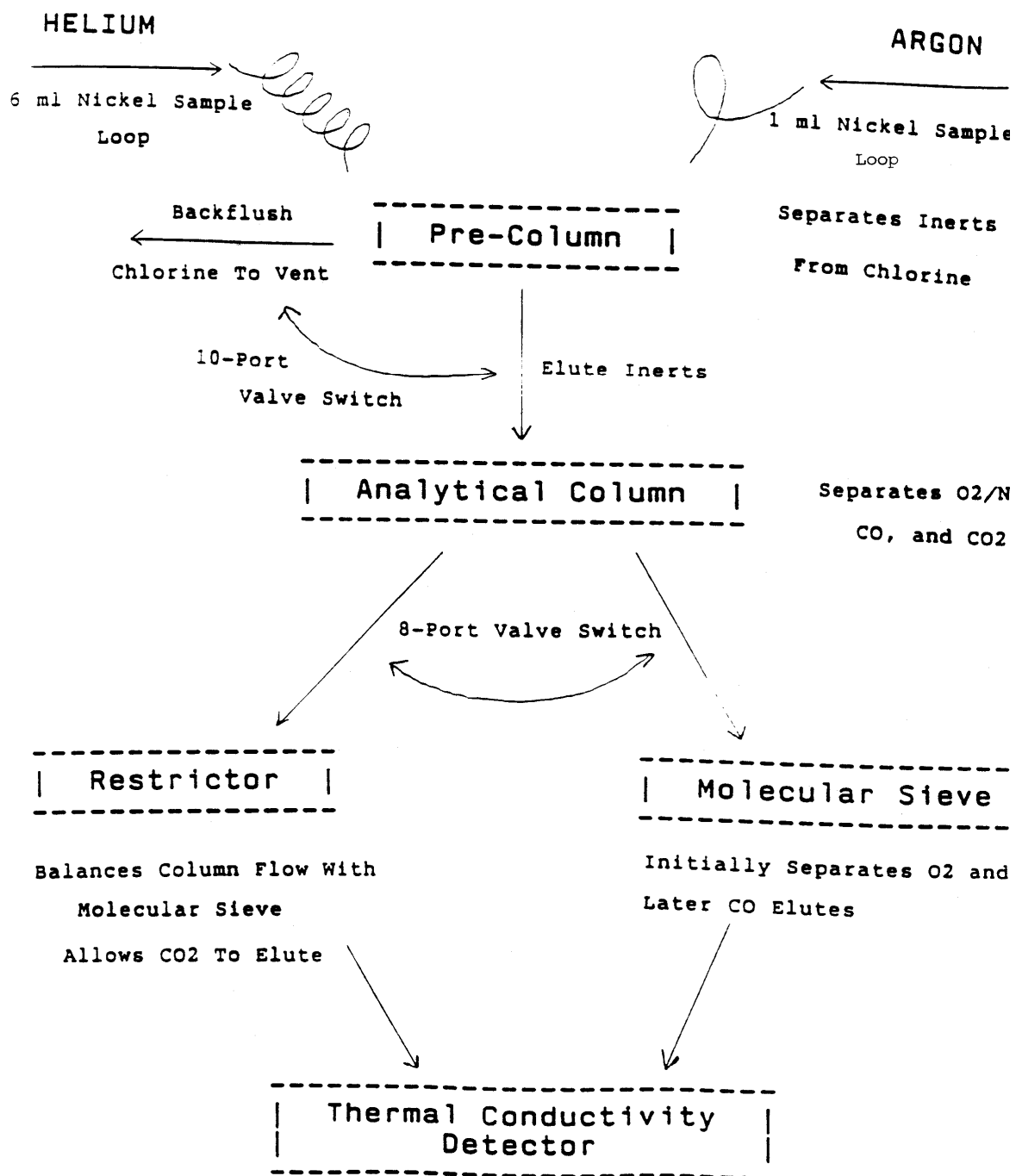


FIGURE 2: INTEGRATION METHOD USED ON PERCENT ANALYS

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LIST: METH 12

RUN PARAMETERS
ZERO = 10
ATT 2 = 1
CHT SP = 0.5
AR REJ = 0
THRESH = 2
PK WD = 0.10

TIMETABLE EVENTS
  0.001 INTG # = 2
  9.500 PK WD = 0.15
 11.500 INTG # = 9
 12.100 INTG # = -9
 15.000 STOP

CALIBRATION
ESTD
REF % RTW: 5.000 NON-REF % RTW: 5.000

LEVEL: 1 RECALIBRATIONS: 1

CAL#   RT      LV      AMT      AMT/AREA
  1     4.966    1  2.5000E-01  1.5463E-06
  2     6.165    1  9.9600E-01  1.3207E-05
  3     6.860    1  4.0300E+00  1.6564E-05
  4    10.746    1  4.9900E-01  1.6893E-05
  5    13.598    1  5.0000E-01  1.7546E-05

CAL#   NAME
  1   % HYDROGEN
  2   % OXYGEN
  3   % NITROGEN
  4   % CARBON DIOXIDE
  5   % CARBON MONOXID

INTEGRATION PLOT TYPE ..... FILTERED

RUN DATA STORAGE
Store signal data ..... NO
Store processed peaks ..... NO

CALIBRATION OPTIONS
RF of uncalibrated peaks .... 0.0000E+00
Calibration fit ..... P
Disable post-run RT update .. YES
SAMPLE AMT ..... 0.0000E+00
MUL FACTOR ..... 1.0000E+00

REPORT OPTIONS
Suppress local report ..... NO
HEIGHT% report ..... NO
Report title:
NON-CONDENSABLES IN 95% CHLORINE
Amount label ..... PERCENT
Report uncalibrated peaks ... YES
Extended report ..... YES

POST-RUN LIST OPTIONS
Store post-run report ..... NO
External post-run report .... NO
List run parameters ..... NO
List timetable ..... NO
List calibration table ..... NO
List remote method ..... NO
Form-feed before report ..... NO
Form-feed after report ..... NO
Skip perforations in report .. NO
Skip perforations in plot ... NO

HP 5890A GAS CHROMATOGRAPH
LOOP ADDRESS: 2

OVEN TEMP = 90 SETPT = 90
EQUIB TIME = 1.00 CRYO OF
OVEN MAXIMUM = 150
INITIAL TEMP = 90
INITIAL TIME = 0.00

RUN LENGTH = 650.00 MIN

INJ A TEMP = 100 SETPT = 100
INJ B TEMP = 74 SETPT = 50 (OFF)
DET A TEMP = 150 SETPT = 150

FLOW A = 17.1 (Ar-CH4)
FLOW B = 37.0 (Ar-CH4)

SIGNAL 1 = A
INET FULL RANGE DATA ON
RANGE = 0
ZERO = -60.5
ATTN = 0

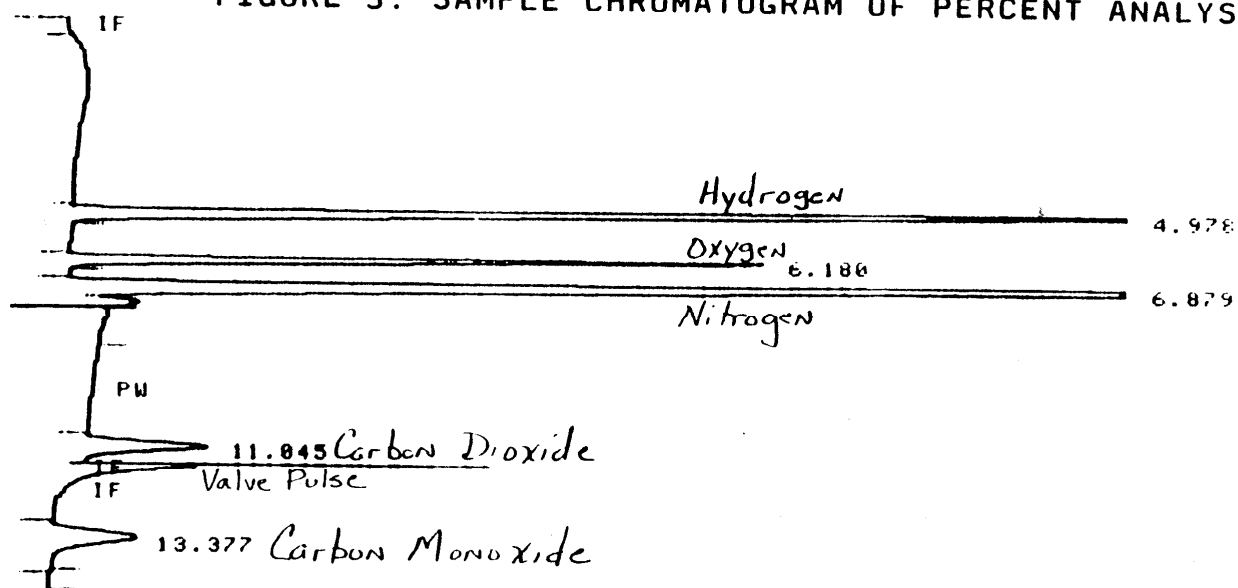
SIGNAL 2 = A
RANGE = 0
ZERO = 0.0
ATTN = 0

DETECTOR A = TCD (ON) POLARITY =

PURGE A = OFF
ON TIME = 0.00 OFF TIME = 1.50
PURGE B = OFF
ON TIME = 7.40 OFF TIME = 11.50

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FIGURE 3: SAMPLE CHROMATOGRAM OF PERCENT ANALYSIS



NON-CONDENSABLES IN 95% CHLORINE

ESTD-AREA

RT	TYPE	AREA	WIDTH	HEIGHT	CALC	PERCENT	NAME
4.978	PB	163604	.151	18013	1	.253	% HYDROGEN
6.180	BB	76625	.135	9429	2	1.012	% OXYGEN
6.879	PV	247029	.185	22220	3R	4.092	% NITROGEN
11.045	I BP	28507	.286	1662	4	.482	% CARBON DIOXIDE
13.377	PB	28233	.401	1173	5	.495	% CARBON MONOXIDE

FIGURE 4:

VALVING DIAGRAM

Prior To The Start Of The Run

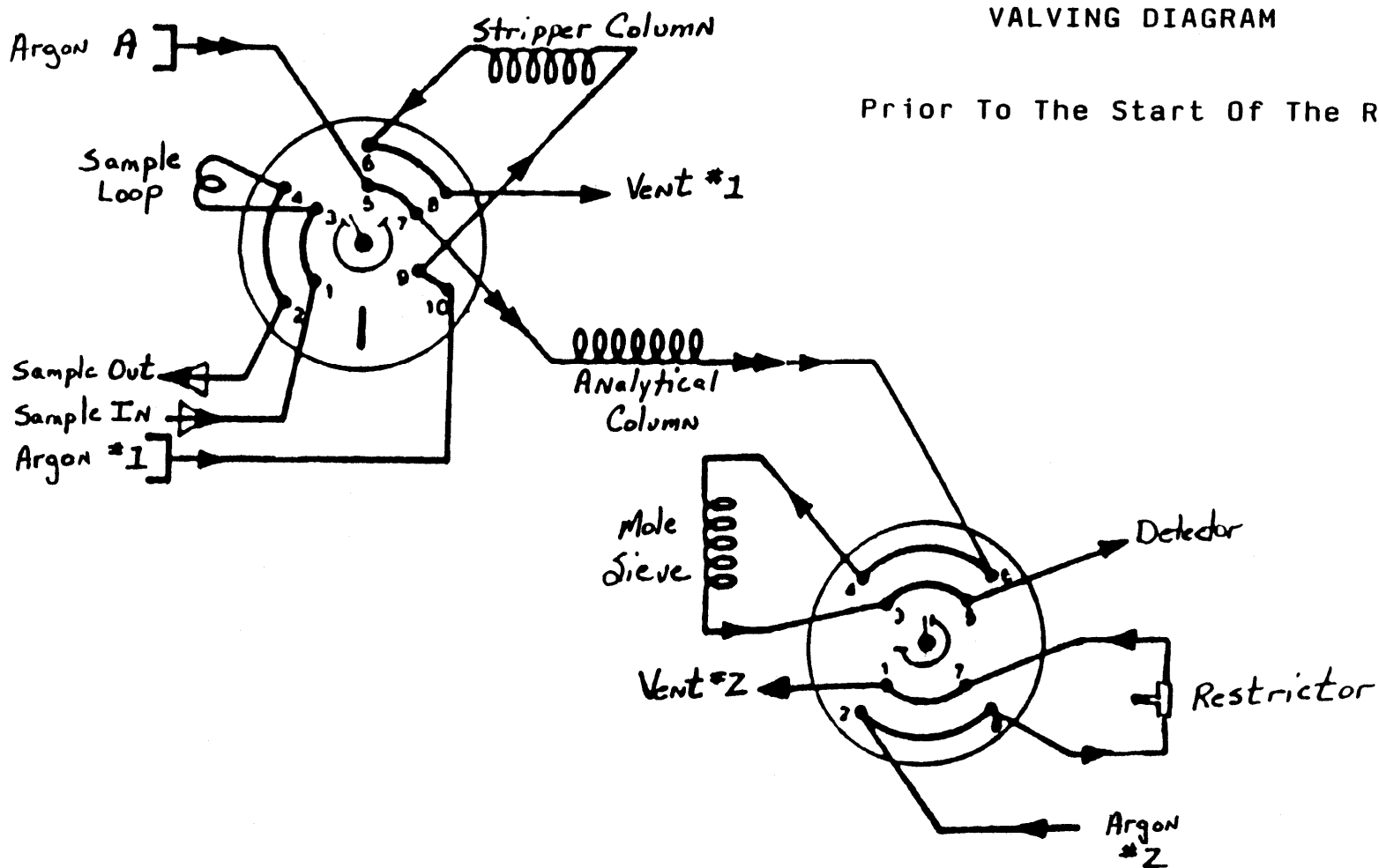


FIGURE 5:
VALVING DIAGRAM
After Start Of Run

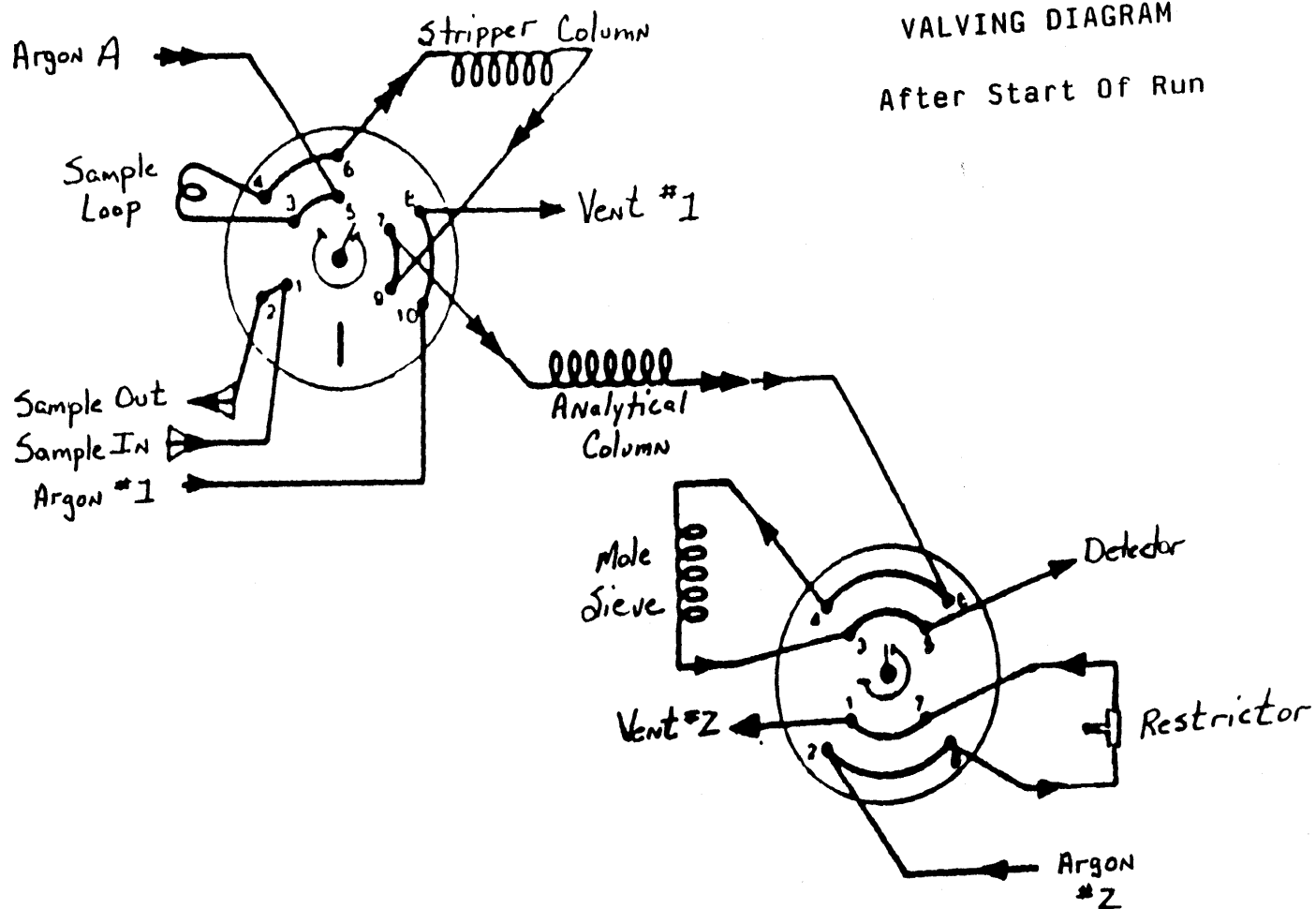


FIGURE 6:

VALVING DIAGRAM

Stripper Column Is Being Backflushed

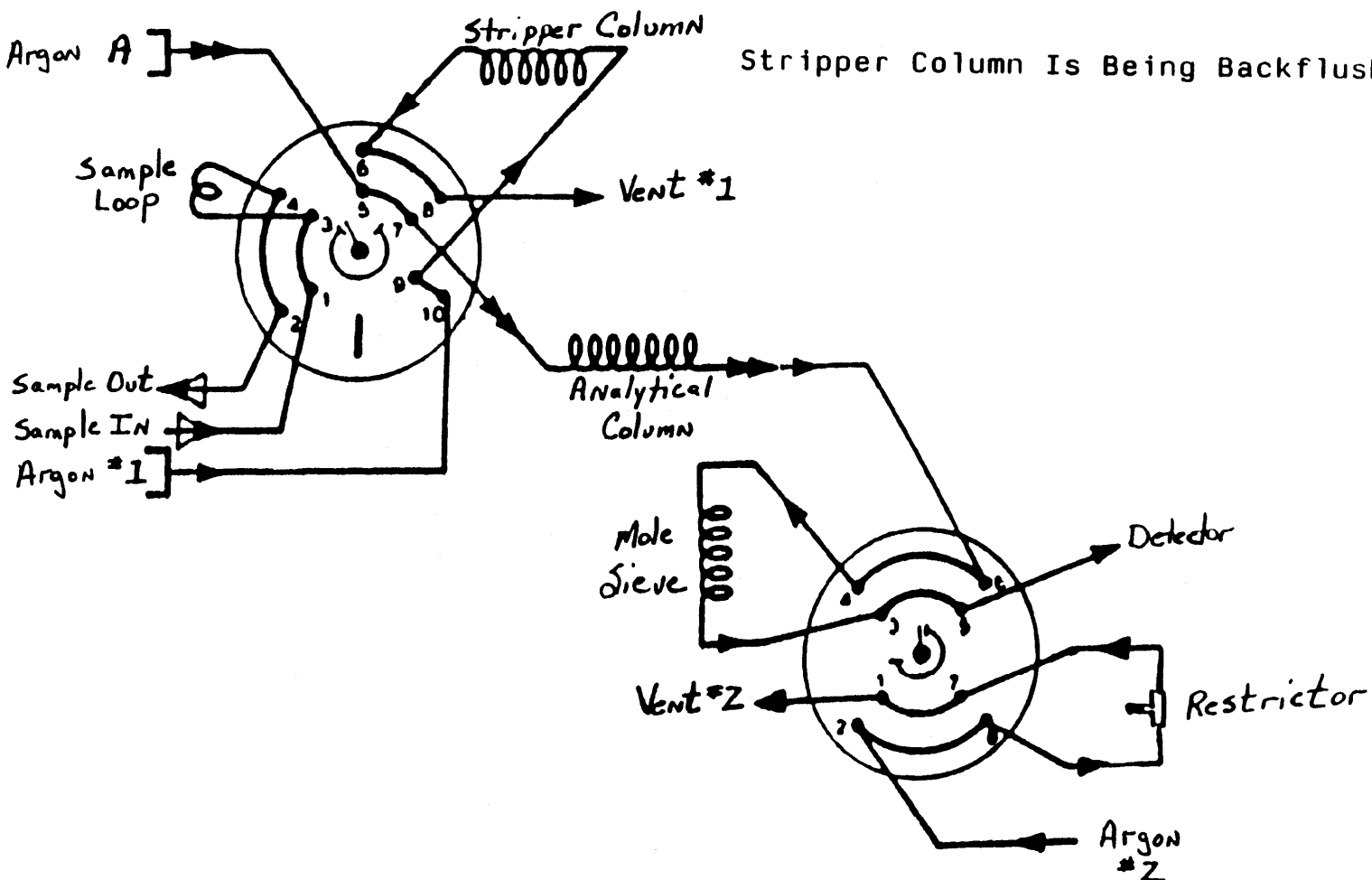


FIGURE 7:

VALVING DIAGRAM

Mole Sieve Is Isolated
And Restrictor Is Inline

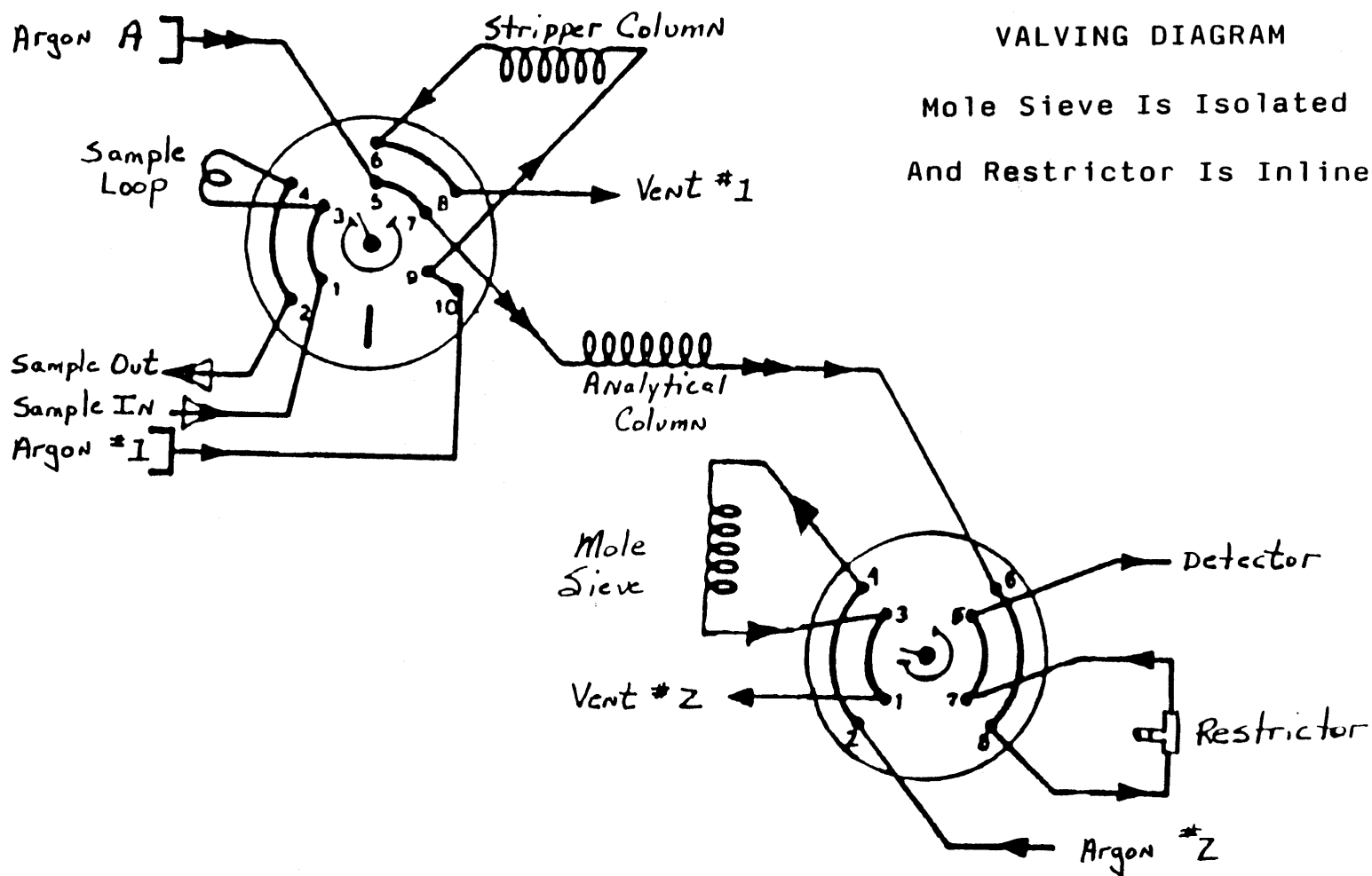


FIGURE 8:

VALVING DIAGRAM

At The End Of The Run

