

2008 User Conference & Technology Fair

Basic Chromatography

Darryl D. Hazlett
Sales Manager GC, FTNIR, and
Analytical Systems
3/27/08





What is an Analyzer

Electronics



What is an Analyzer





What is an Analyzer





What's the Ruler



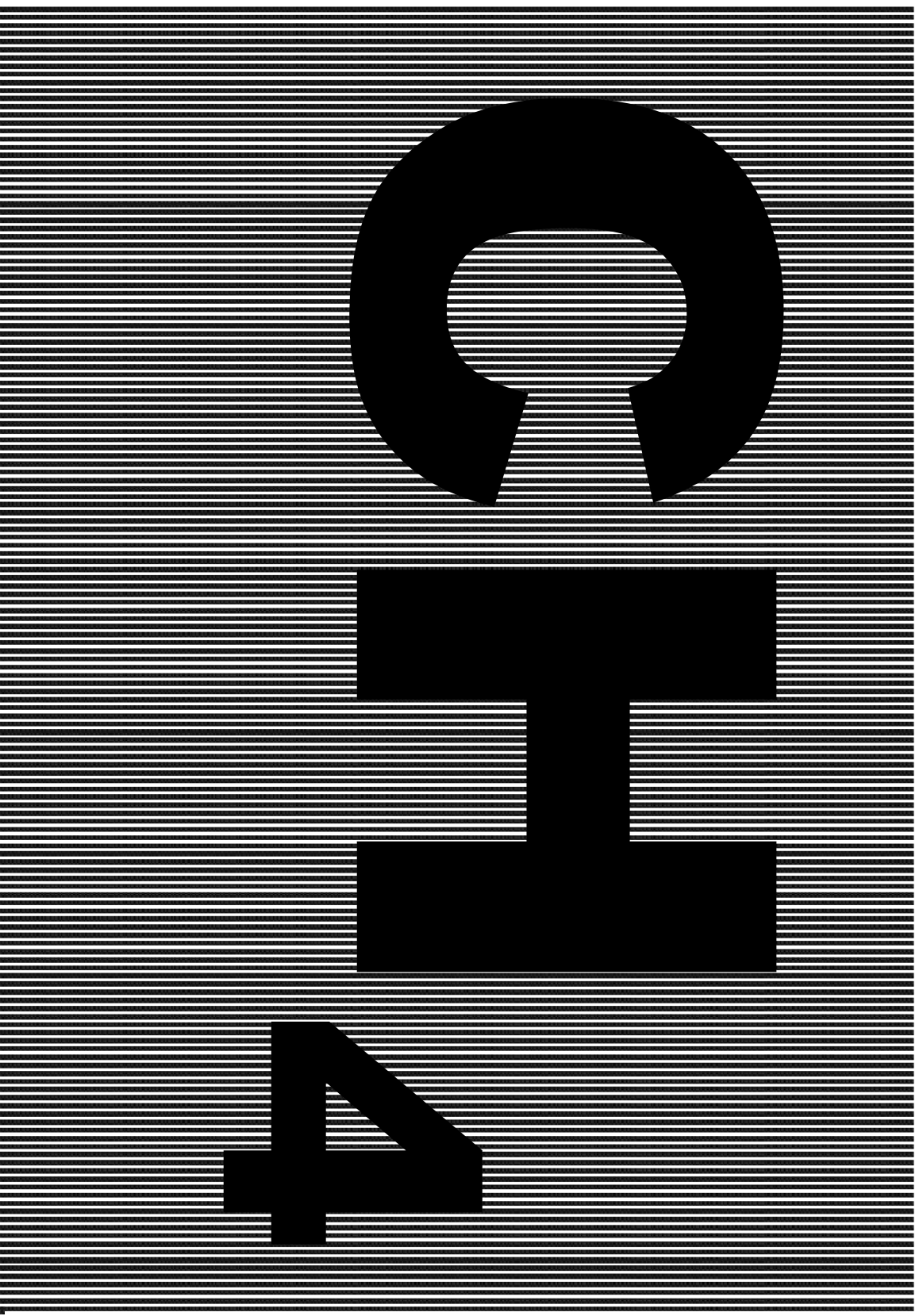


How much

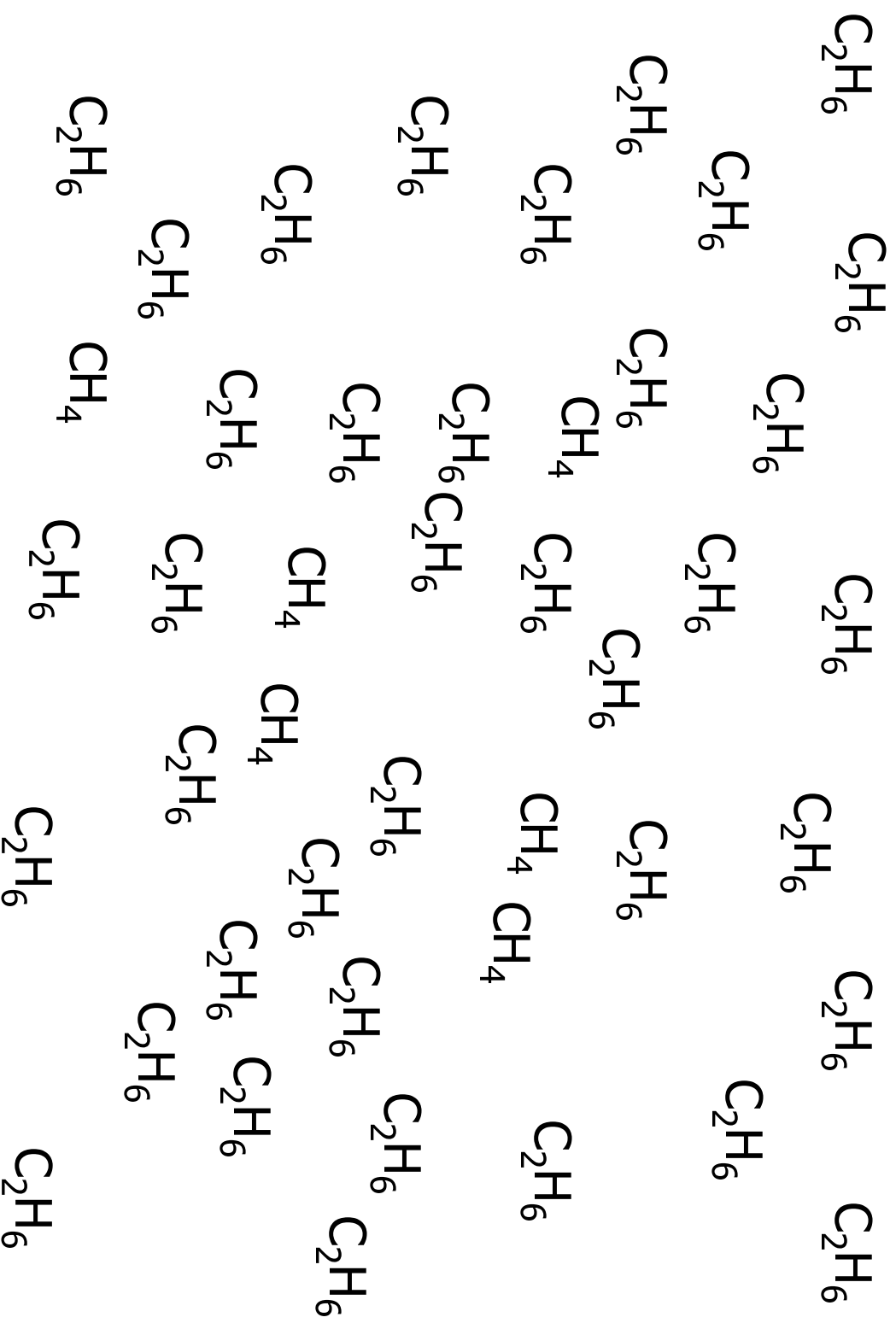
CE4



What is it in



It all makes a difference





Chromatography

❖ “Chromo” “graph”

❖ From the Greek words for

❖ Color Writing



Chromatography

- ❖ There are many types of Chromatographs.
- ❖ Chromatography is a SEPARATION technique of a mixture.
- ❖ Most Separations methods rely on Physical differences of the components.
- ❖ Simplest is Paper Chromatography.
 - Paper is the **Stationary Phase**
 - **Water is the mobile phase**
- ❖ The Differences are the Phases involved.



Demonstration



Chromatography

⇨ The Types of Phases.

- **Gas / Vapor**
- **Liquid**
- **Solid**
 - Could be a solid coated with a liquid.

⇨ What is the Phase(s) involved in a typical Process Gas Chromatograph?

Chromatography

❖ The Types of Phases.

- **Gas / Vapor**
 - **Liquid**
 - **Solid**
 - Could be a solid coated with a liquid.
- ❖ What is the Phase(s) involved in a typical Process Gas Chromatograph?

❖ GLS

❖ Or Simply a GC



FIRST LAW OF GAS CHROMATOGRAPHS



FIRST LAW OF GAS CHROMATOGRAPHS

The sample must be Vapor
or Vaporize (100%) when
injected.



What are the basic parts of a GC?

The Column - examples

HayeSep Q @10 foot

3 Flow Restrictors 1 / 16"

20% OV0-101 on Chromosorb
P-AW 80/100 @1 foot



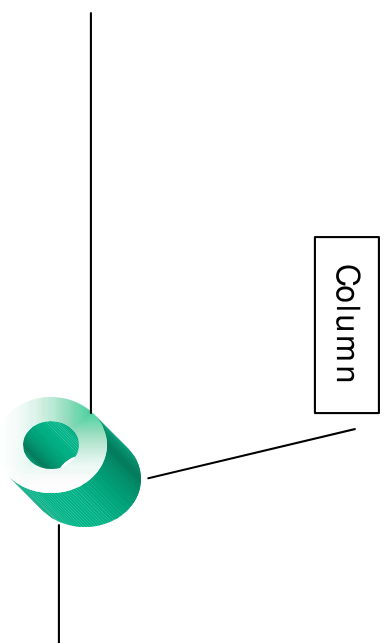
20% OV0-101 on Chromosorb Buffer, Chromosorb P-AW
P-AW 80/100 @8 foot 80/100 @3 foot

The Column

❖ Basic terminology about Columns

- **RETENTION TIME (t_R)**
- **COLUMN BLEED**
- **COLUMN TEMPERATURE LIMITS**
- **COLUMN CAPACITY**

OR – stationary phase



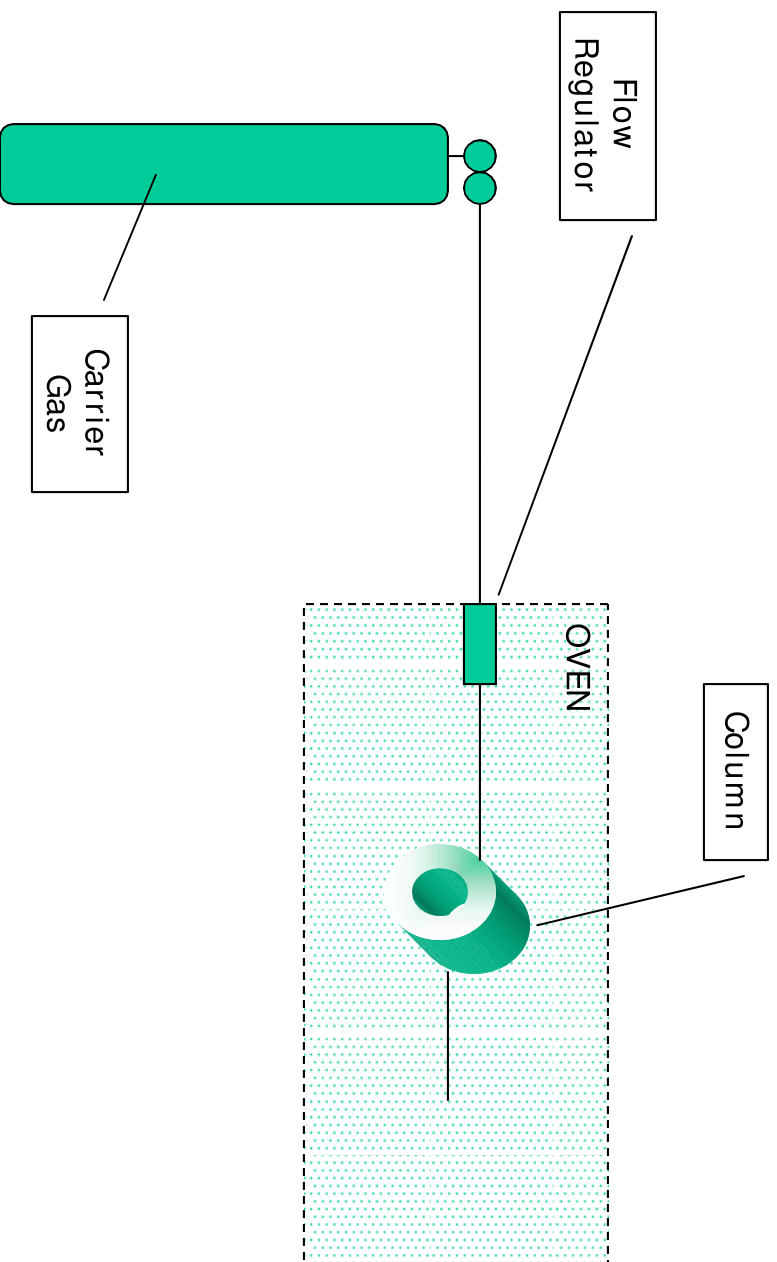
Flow Control

- ❖ The Mobile phase must be constant in flow.
- ❖ Originally Pressure Regulators with Capillary columns to fix flow.
 - **Regulators have been blamed for drift due to temperature sensitivity.**
- ❖ Today options include EPCs – Electronic Pressure Controllers

Flow Control

- ✚ The Mobile phase must be constant in flow .
- ✚ Originally Pressure Regulators with Capillary columns to fix flow .
 - **Regulators have been blamed for drift due to temperature sensitivity.**
- ✚ Today options include EPCs – Electronic Pressure Controllers
- ✚ Oh Yes – let's add a Temperature Stabilizing Zone, some call it an oven...

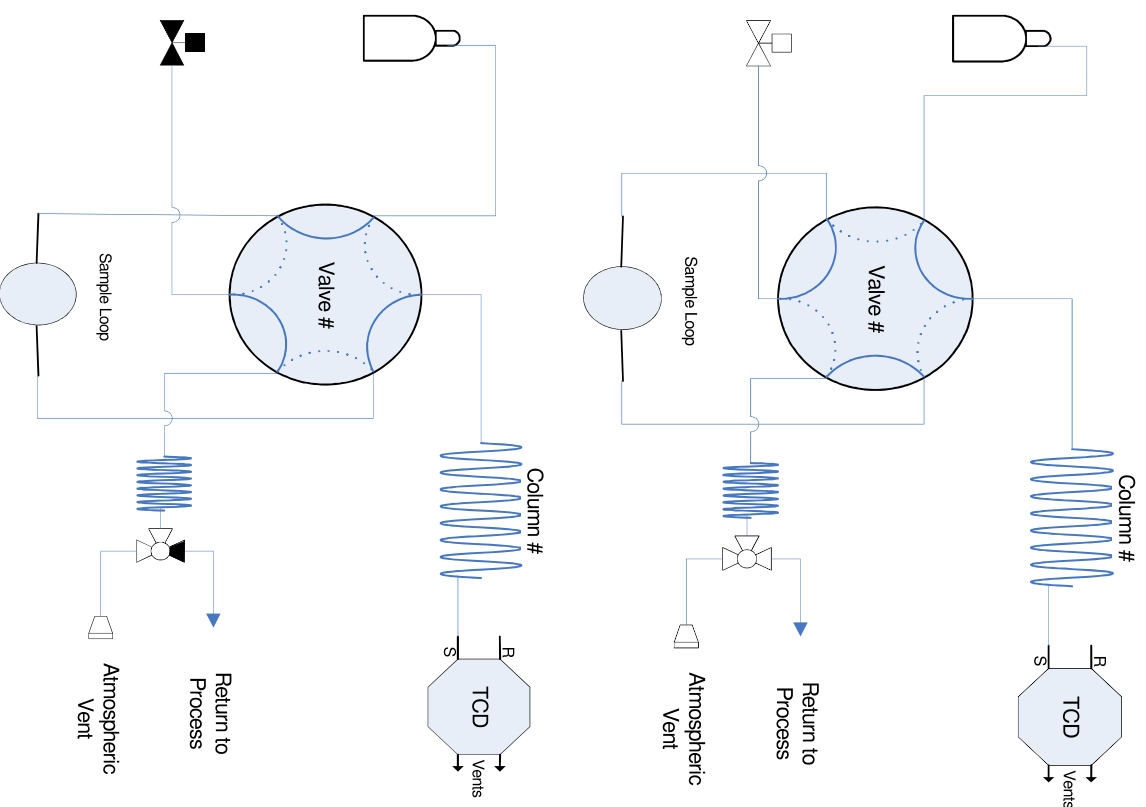
Parts of a Chromatograph – Mobile phase



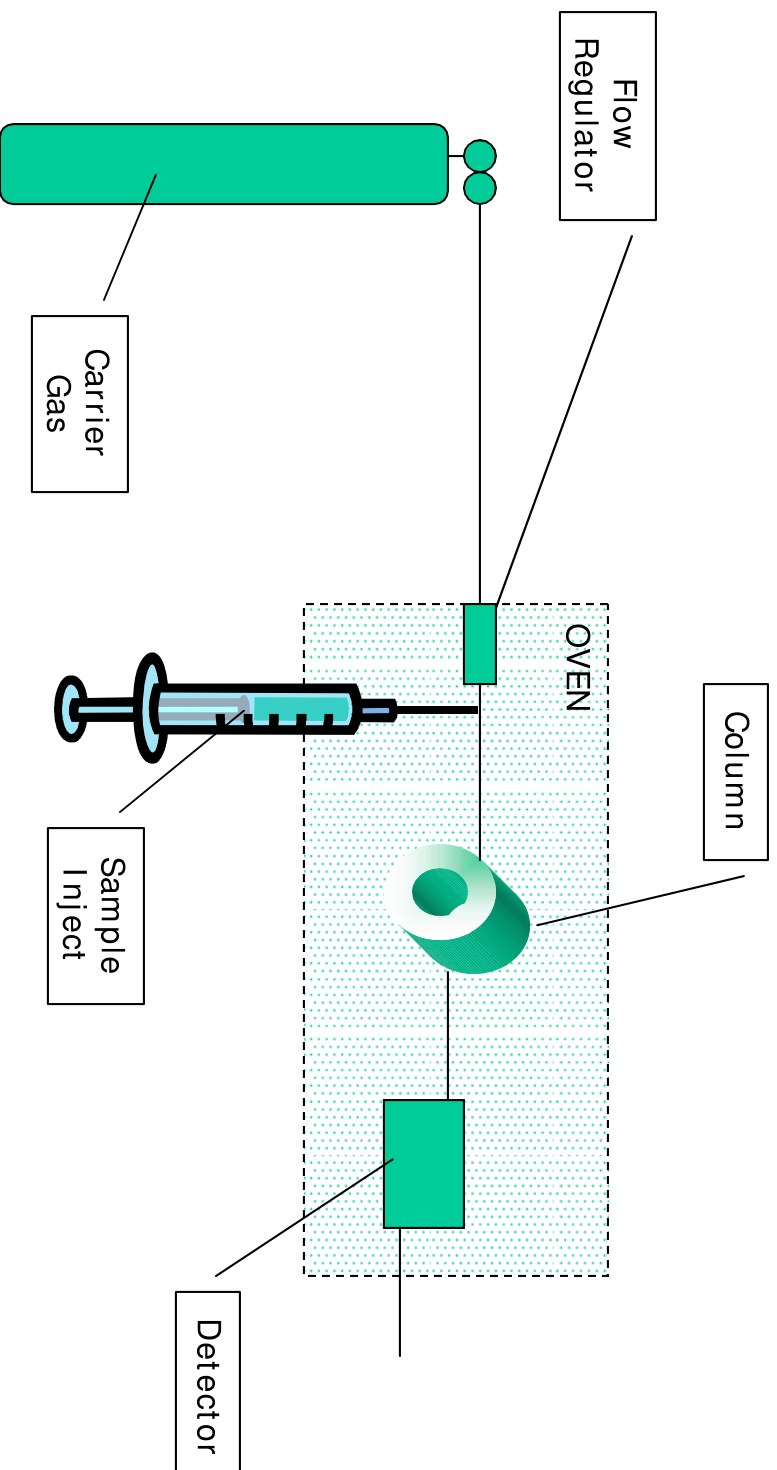
Sample Introduction

❖ Lab units have used syringes to introduce the sample. Volume repeats ok but rate is weak point.

❖ Process GCs typically use a valve with a sample loop. A maintained PGC will have excellent repeatability in both volume and rate.



Parts of a Chromatograph – inject & Detect



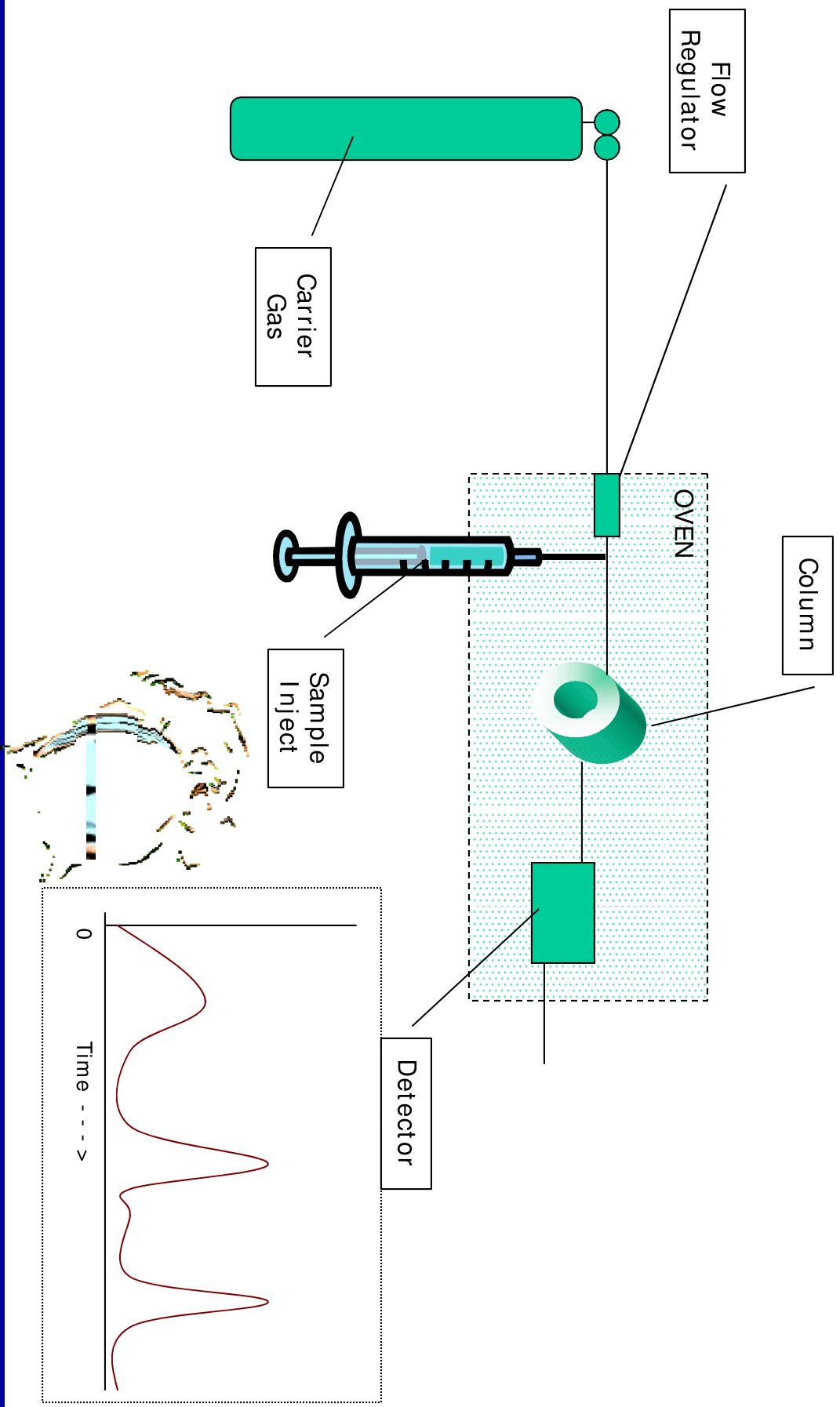
Detector and Timer

❖ We already showed a detector.

- **There are many types for many applications**
- **Most Common in PGCs are**
 - Thermal Conductivity or TCD
 - Measures HC and gases
 - Generally considered a % range
 - Flame Ionization or FID
 - Measures HC or CO & CO₂ with a Methanetor
 - Ranges from % to ppm levels
 - Flame Photometric FPD
 - Sulfur and sulfur bearing compounds
 - Ranges from % to ppm levels
- Details on each to follow later

❖ And a timer – everything needs to be tracked

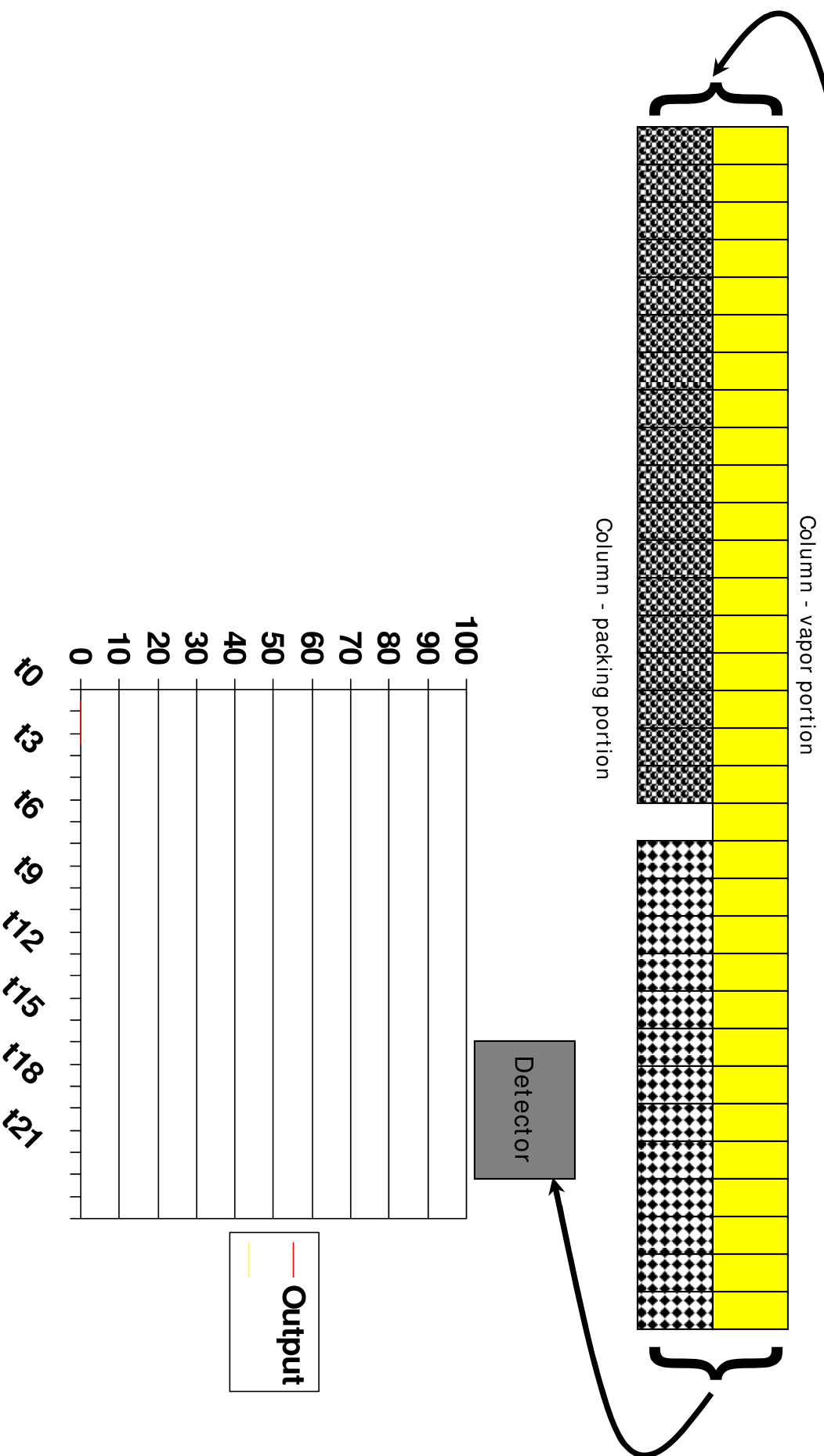
Parts of a Chromatograph





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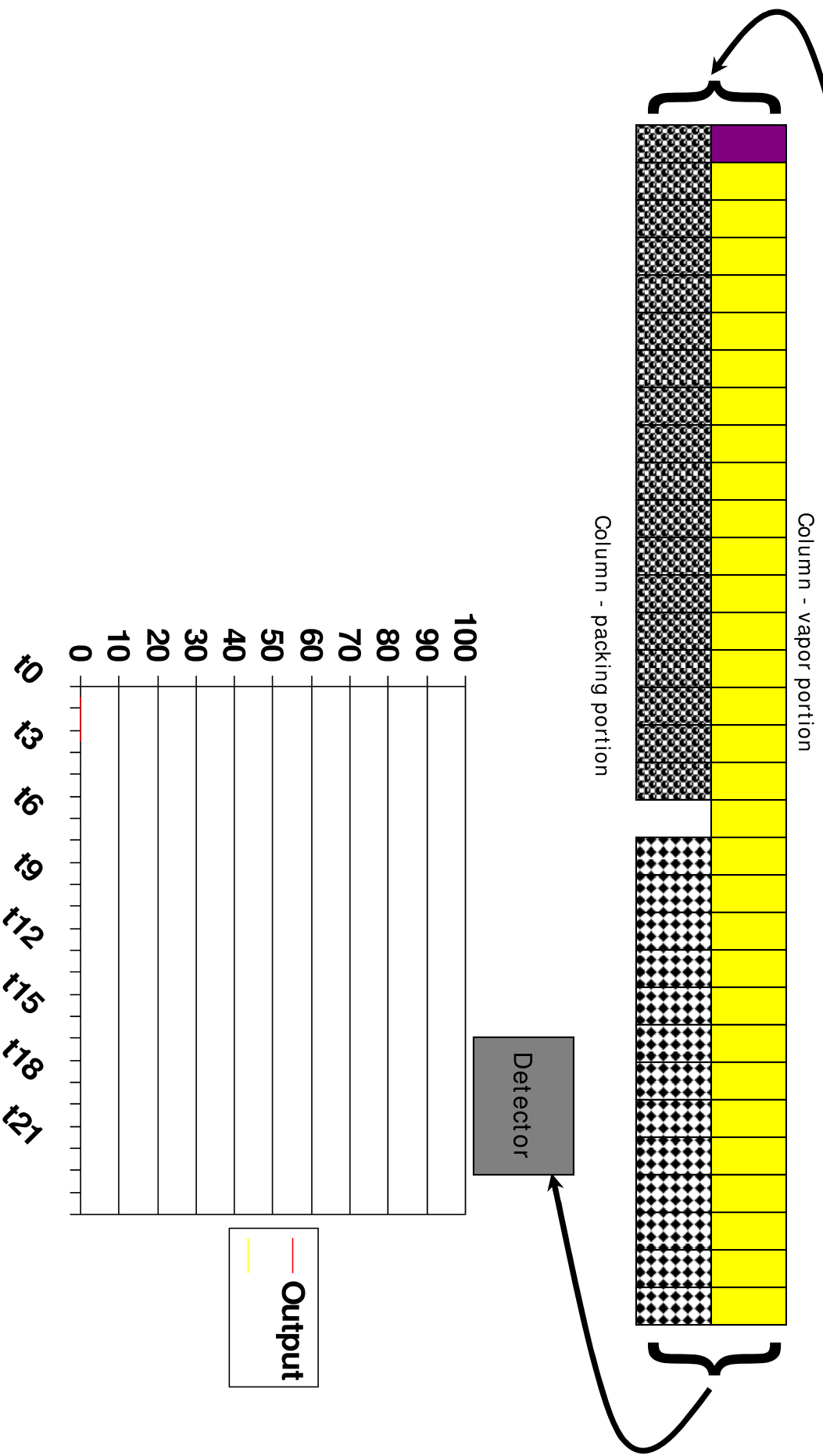
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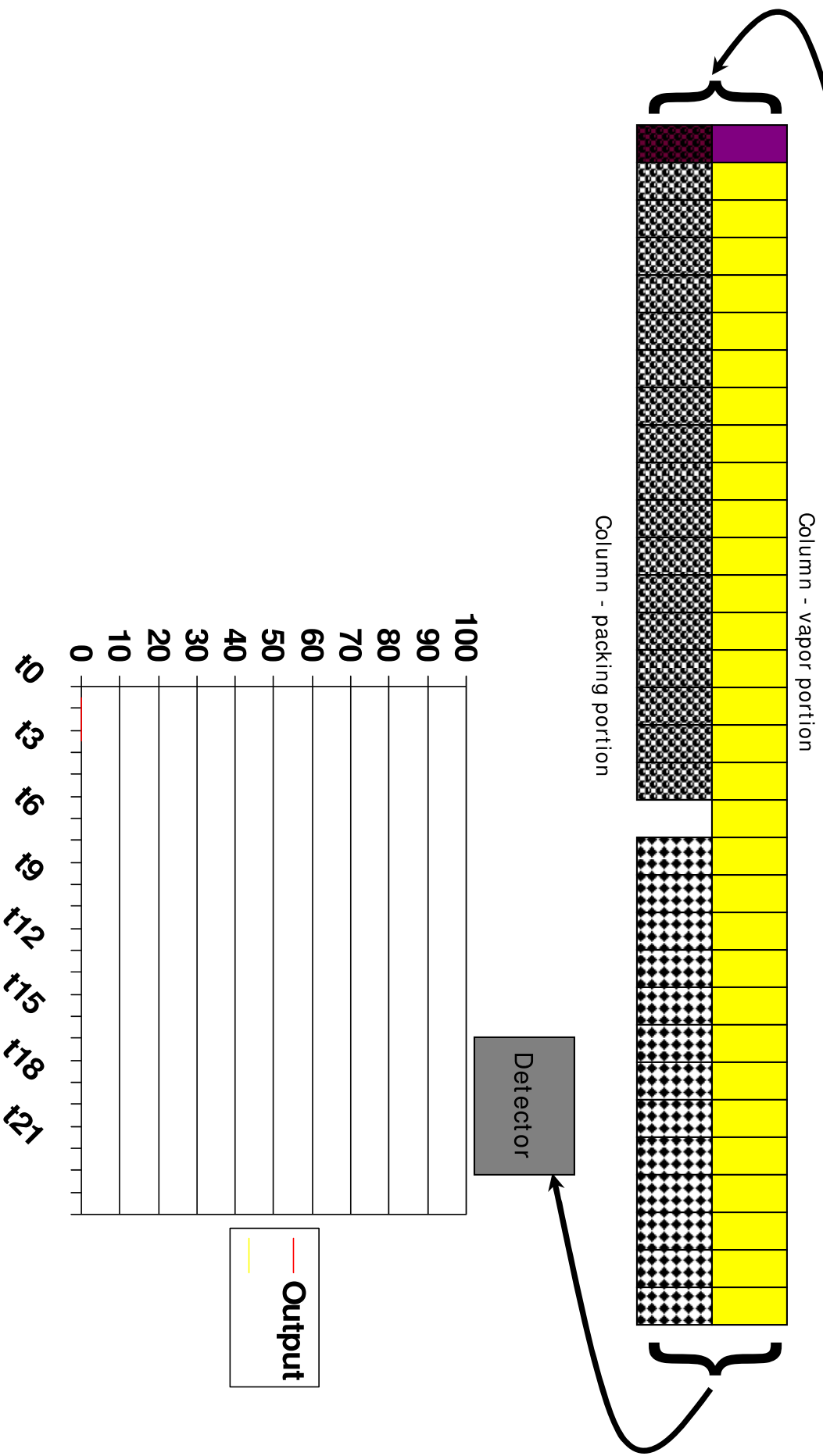
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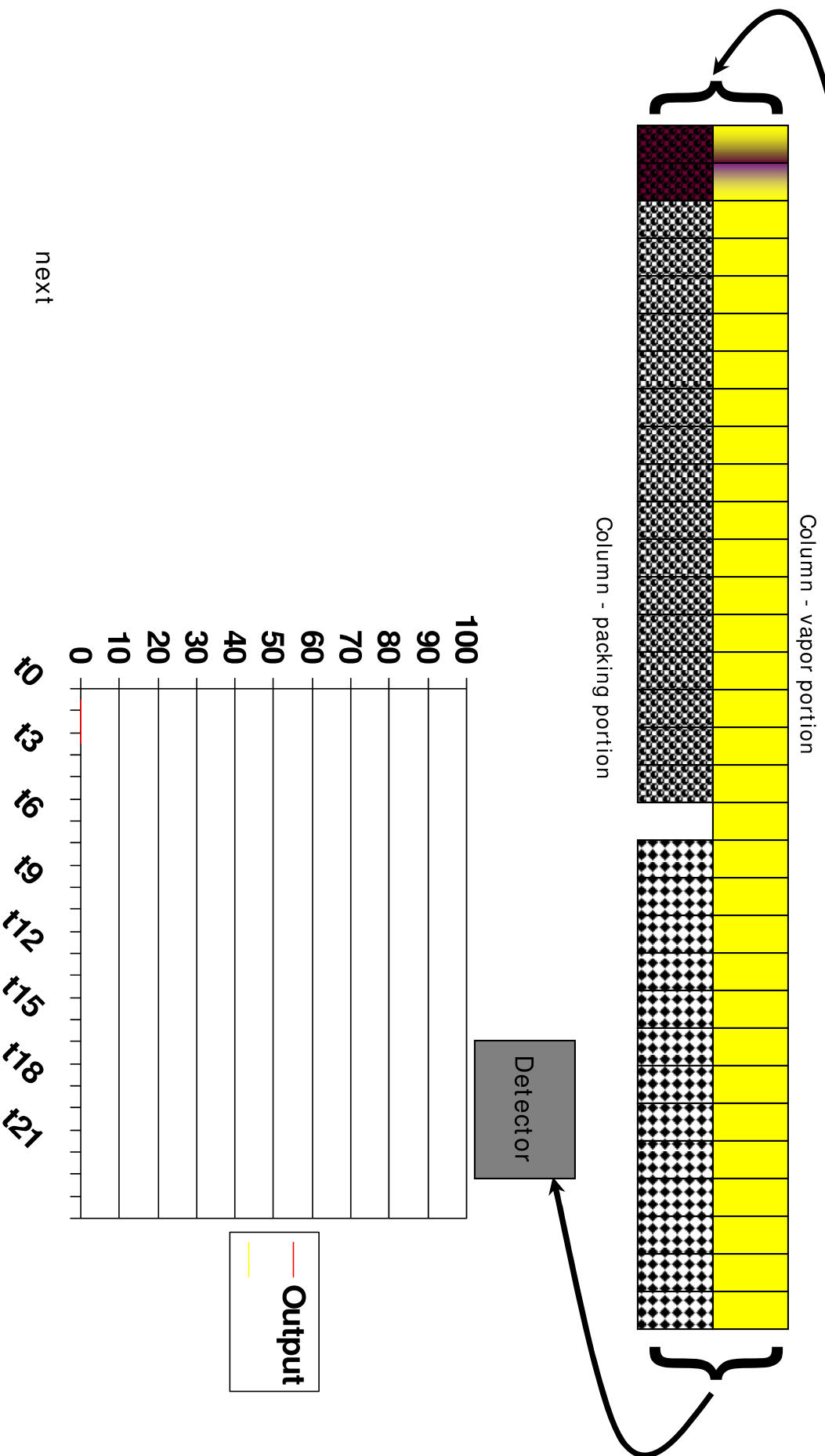
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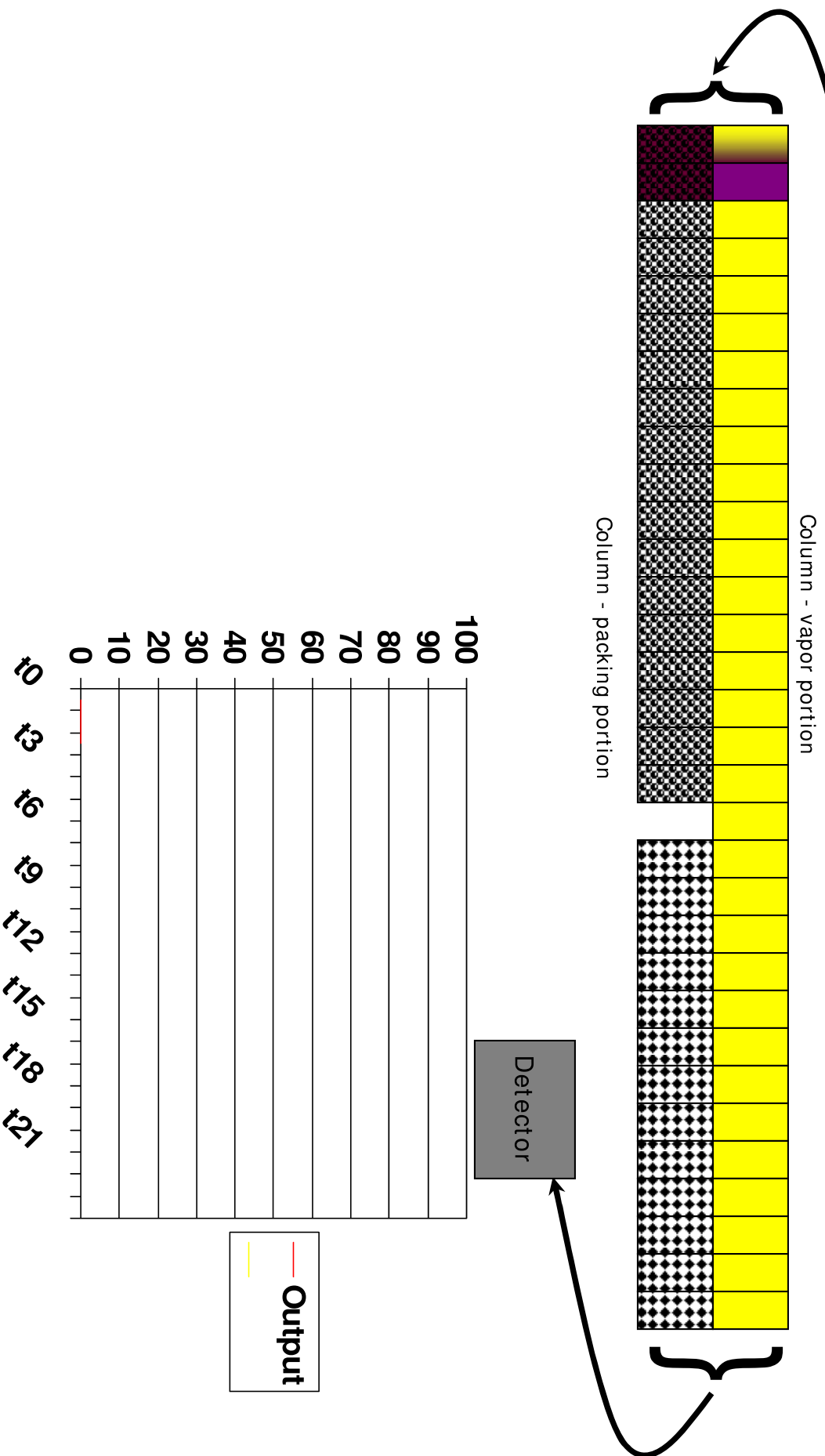
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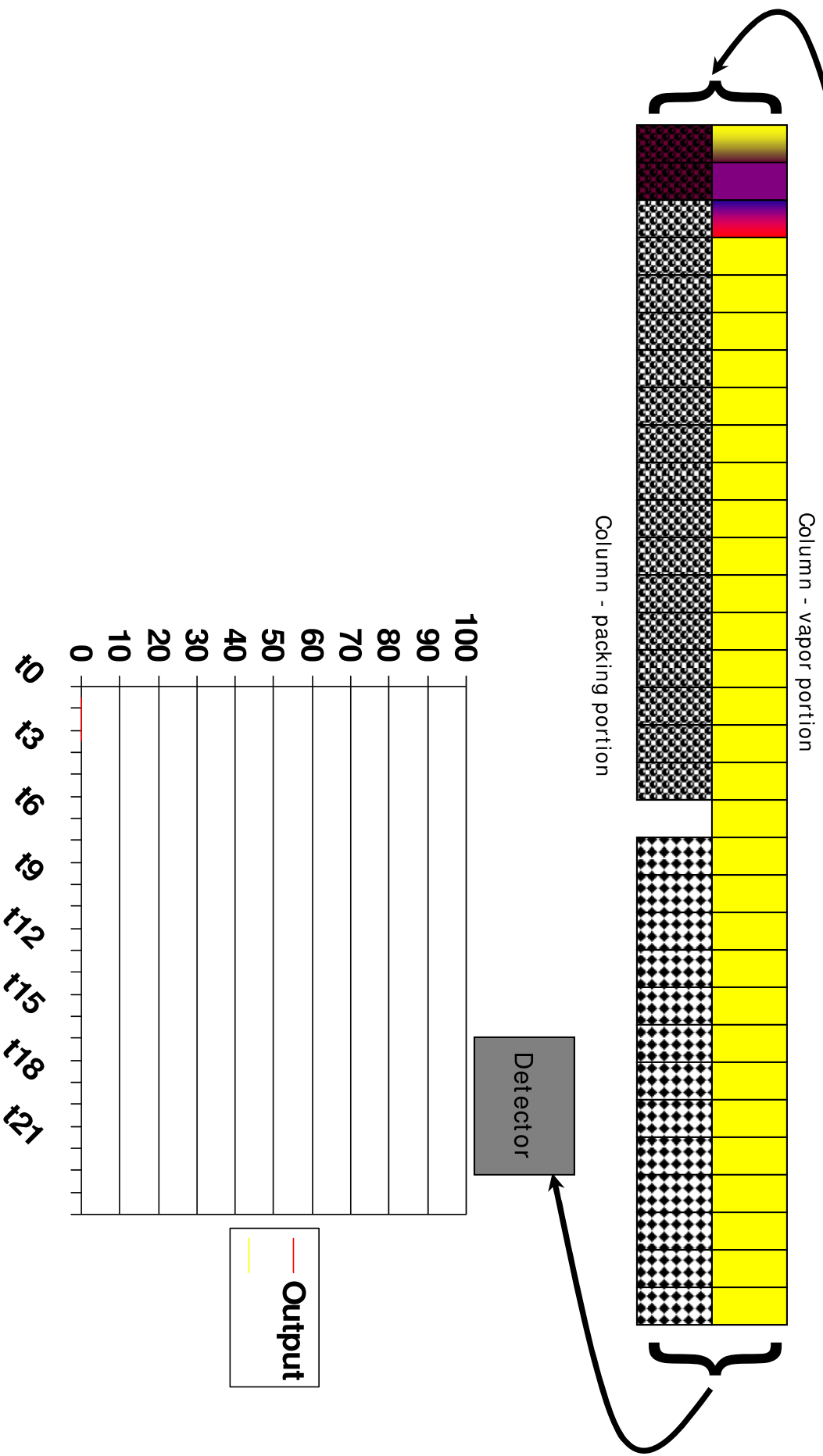
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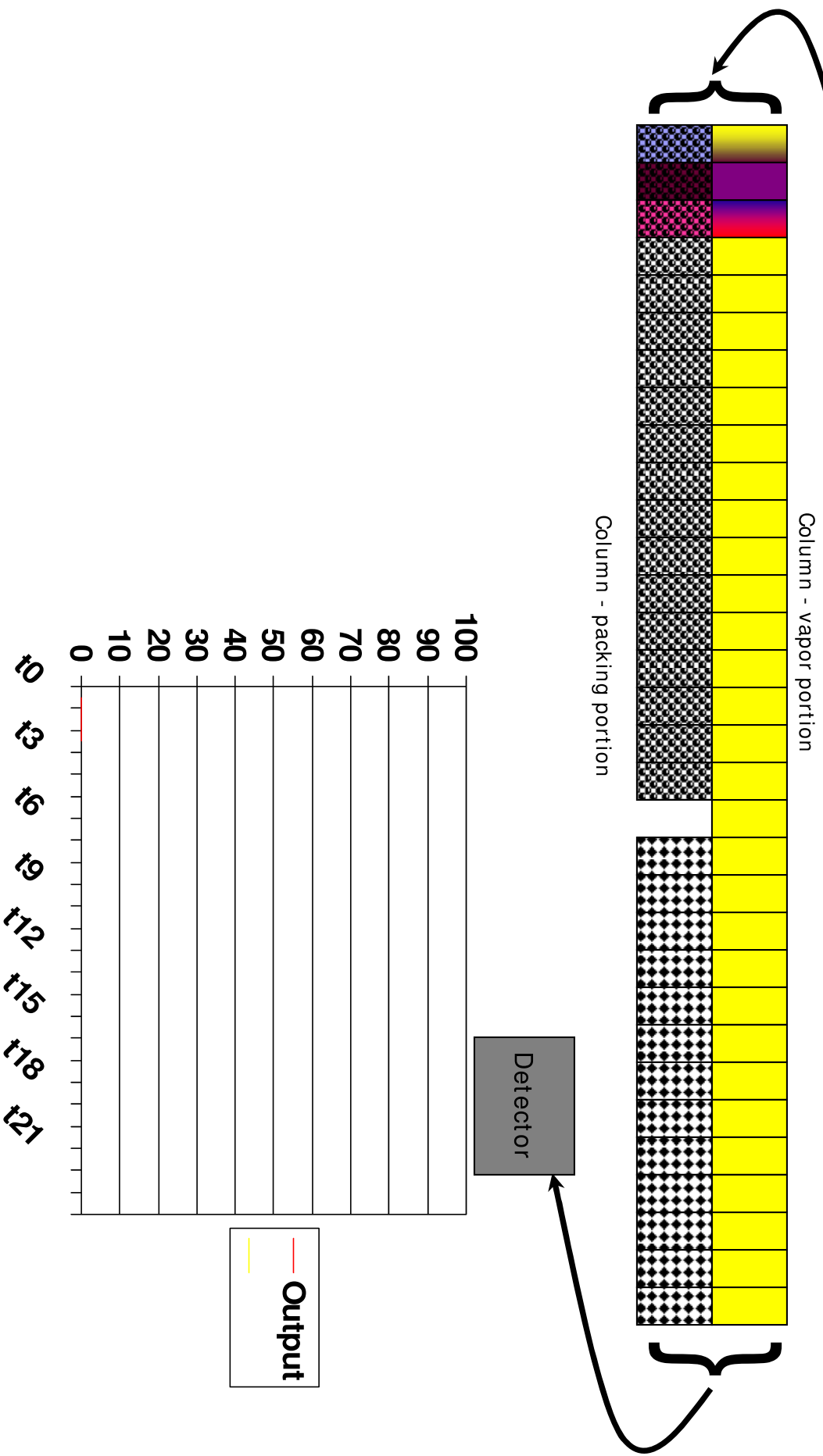
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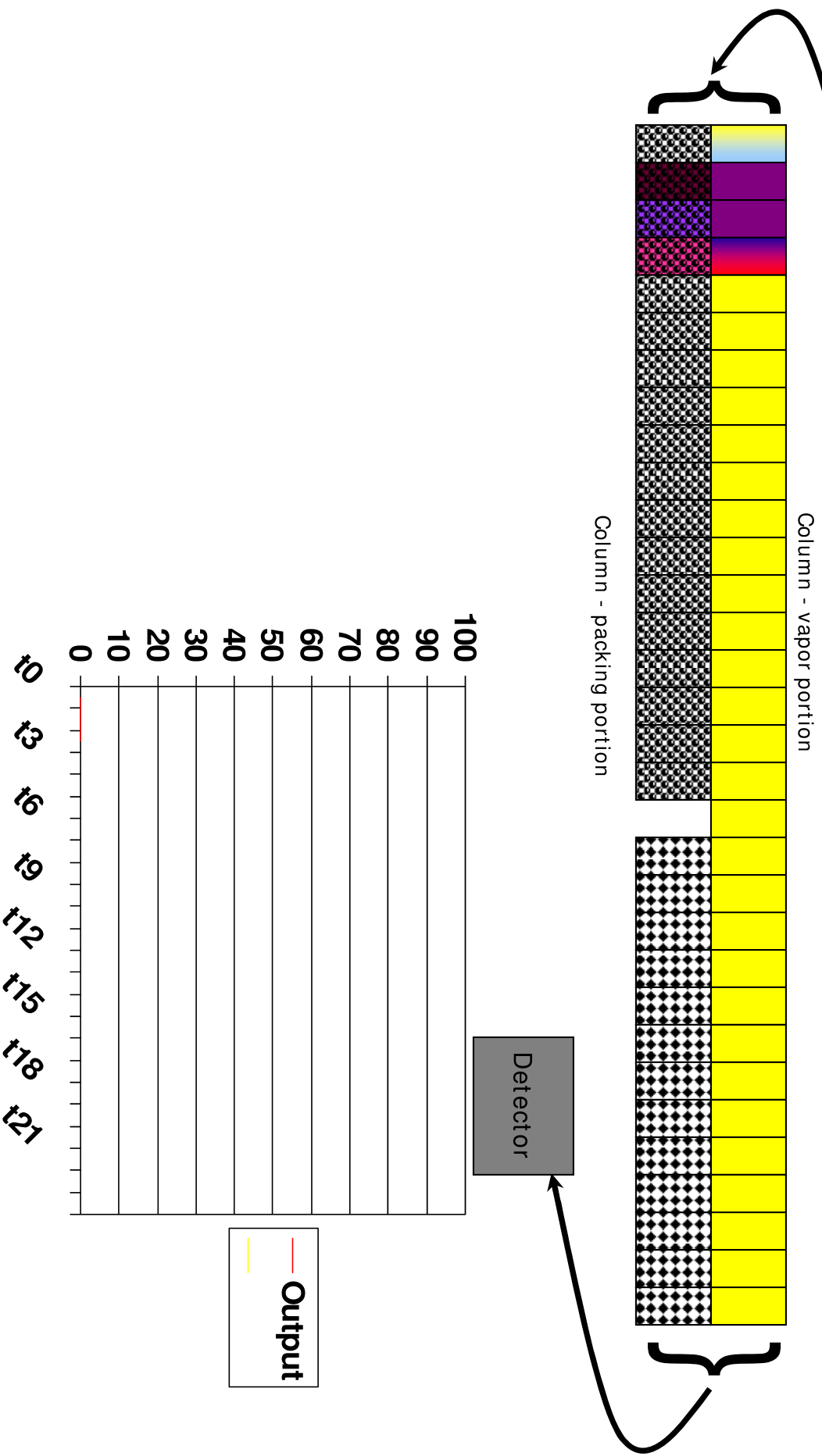
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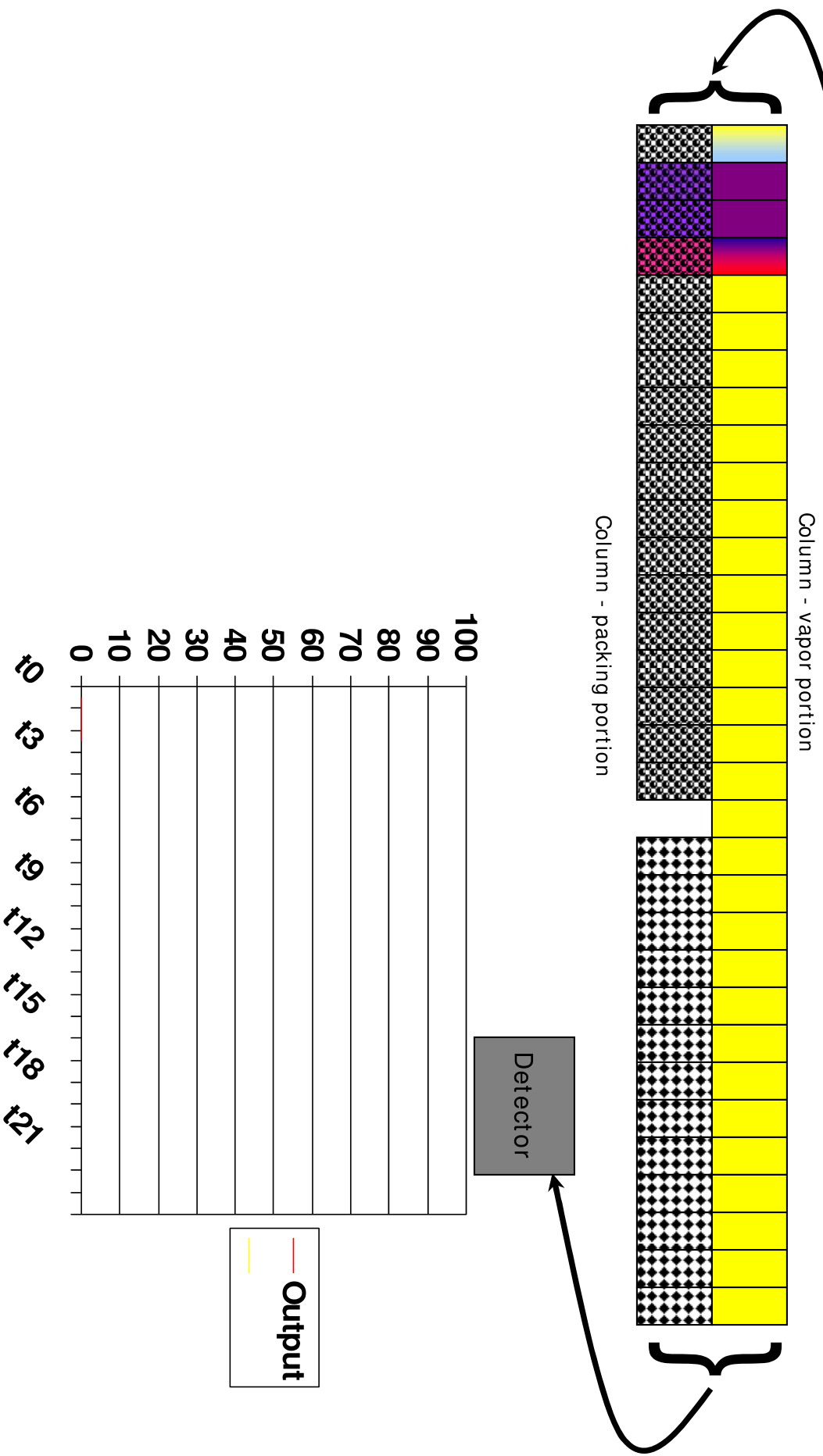
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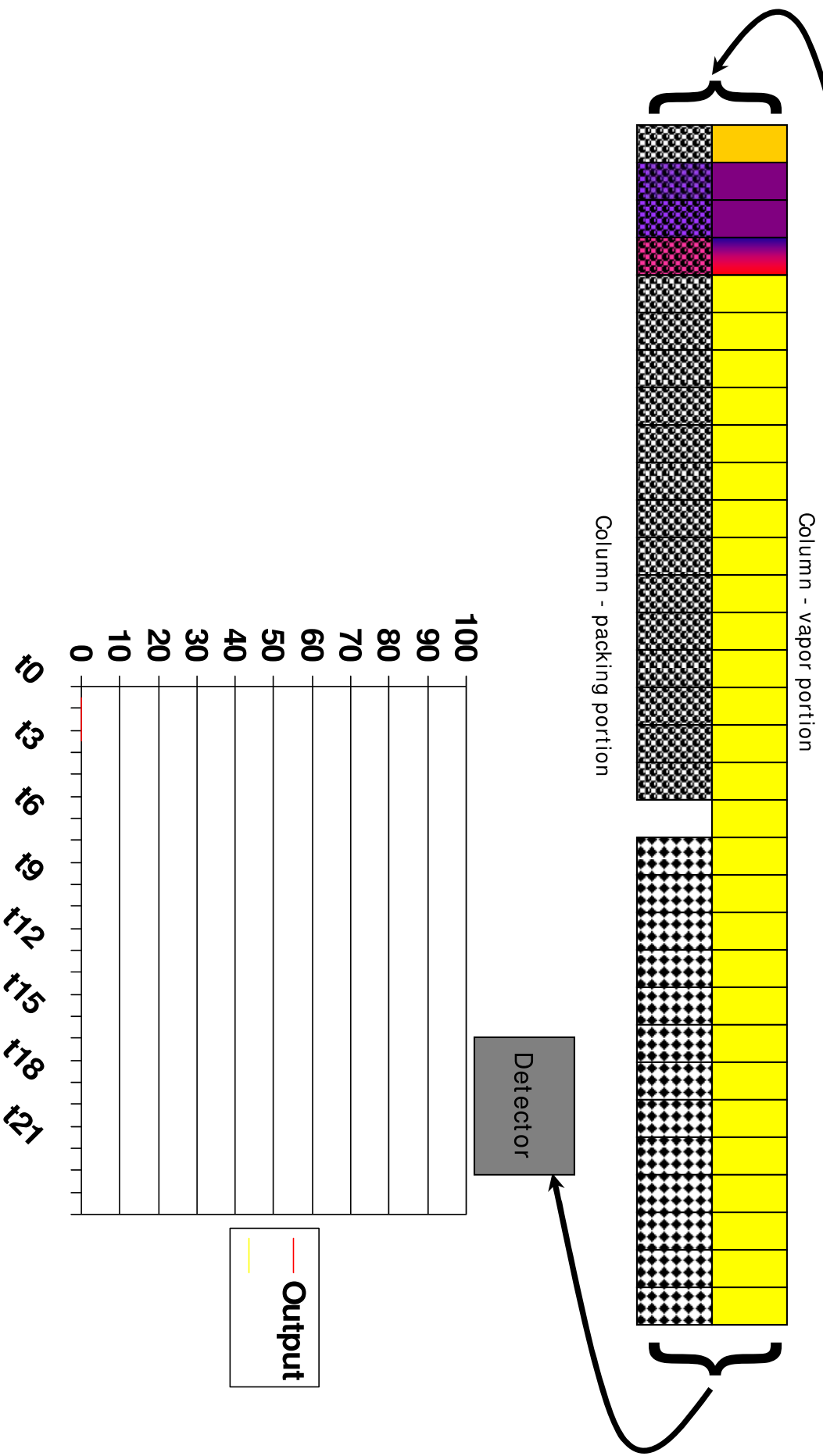
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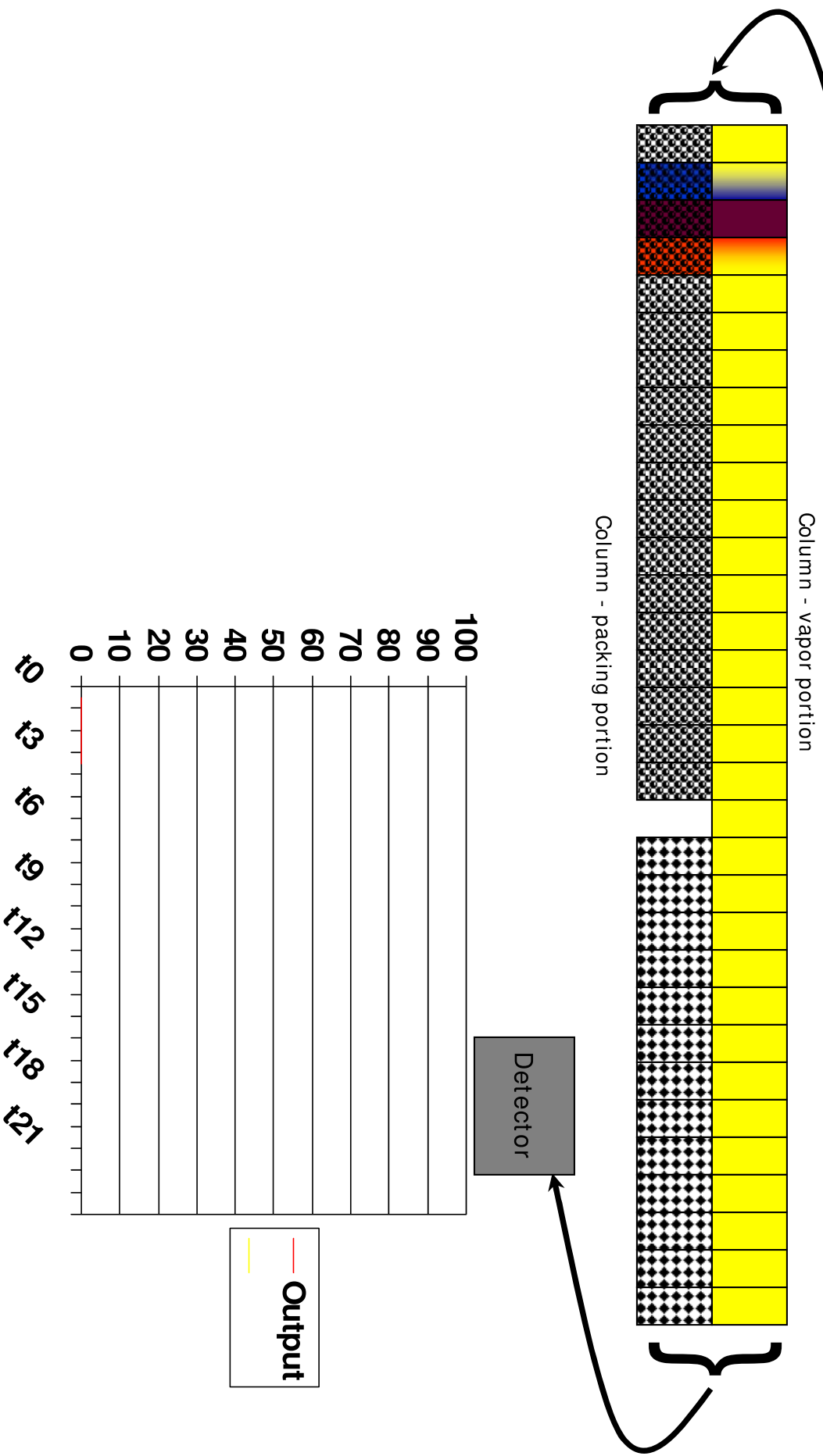
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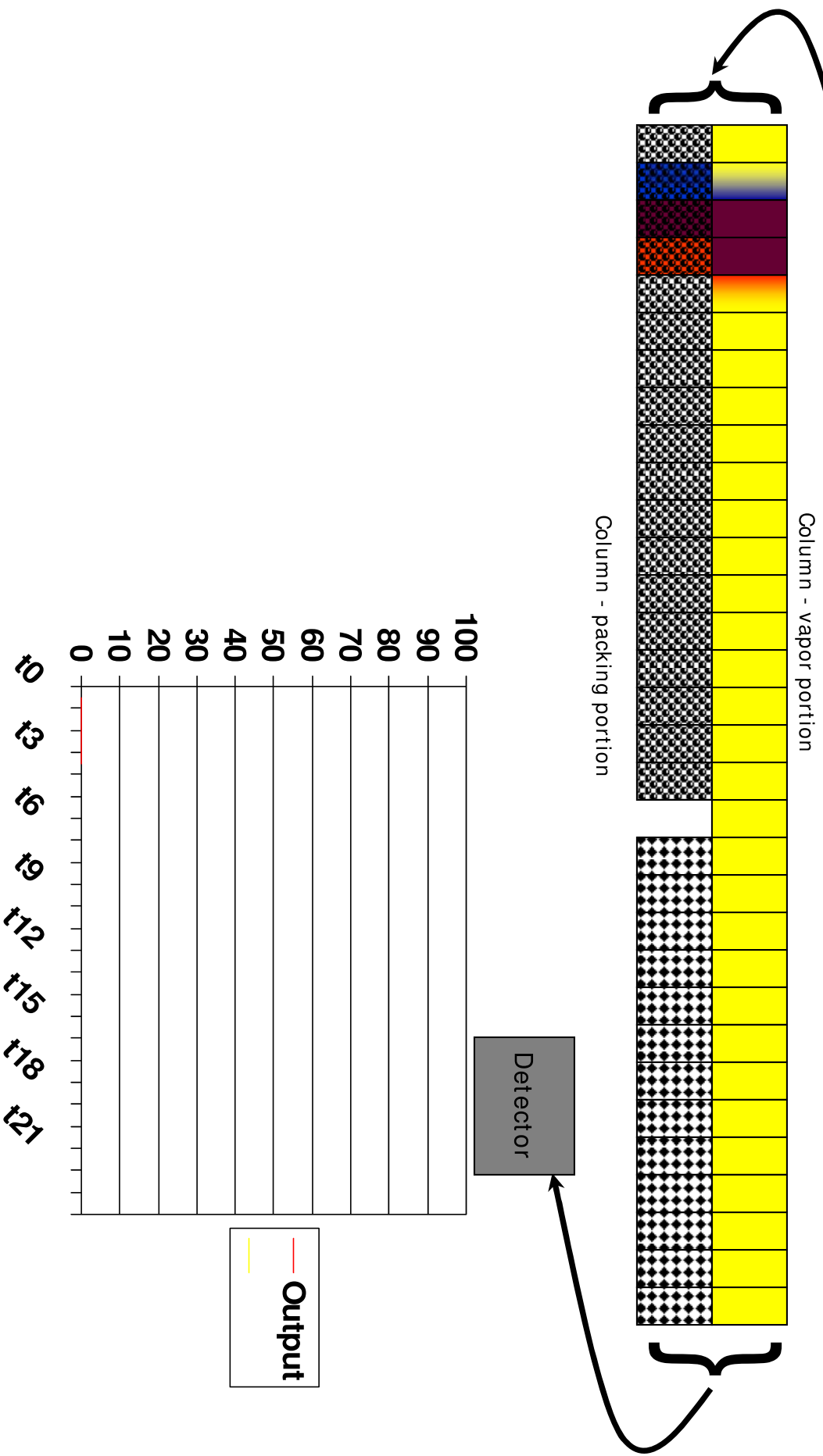
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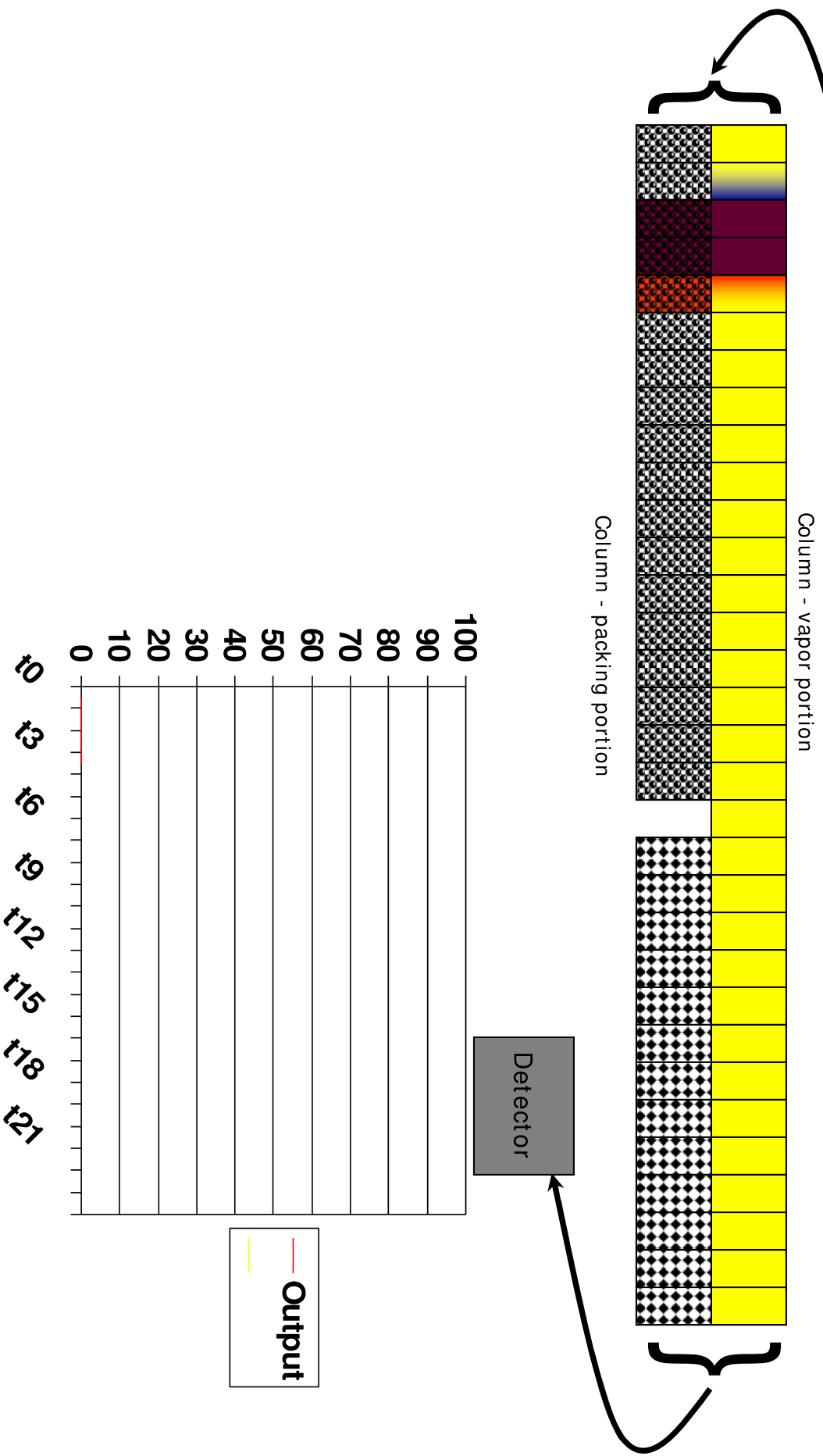
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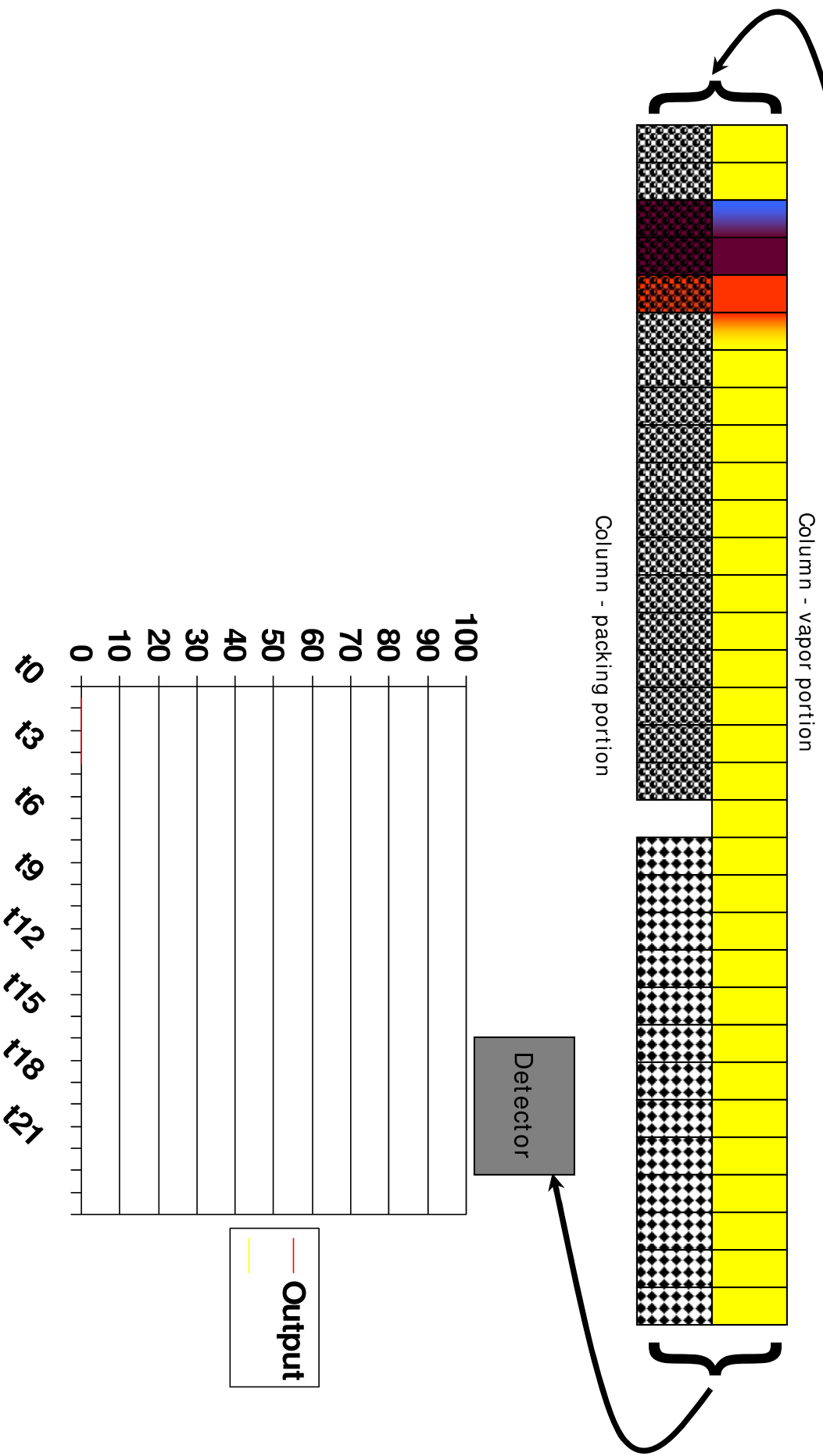
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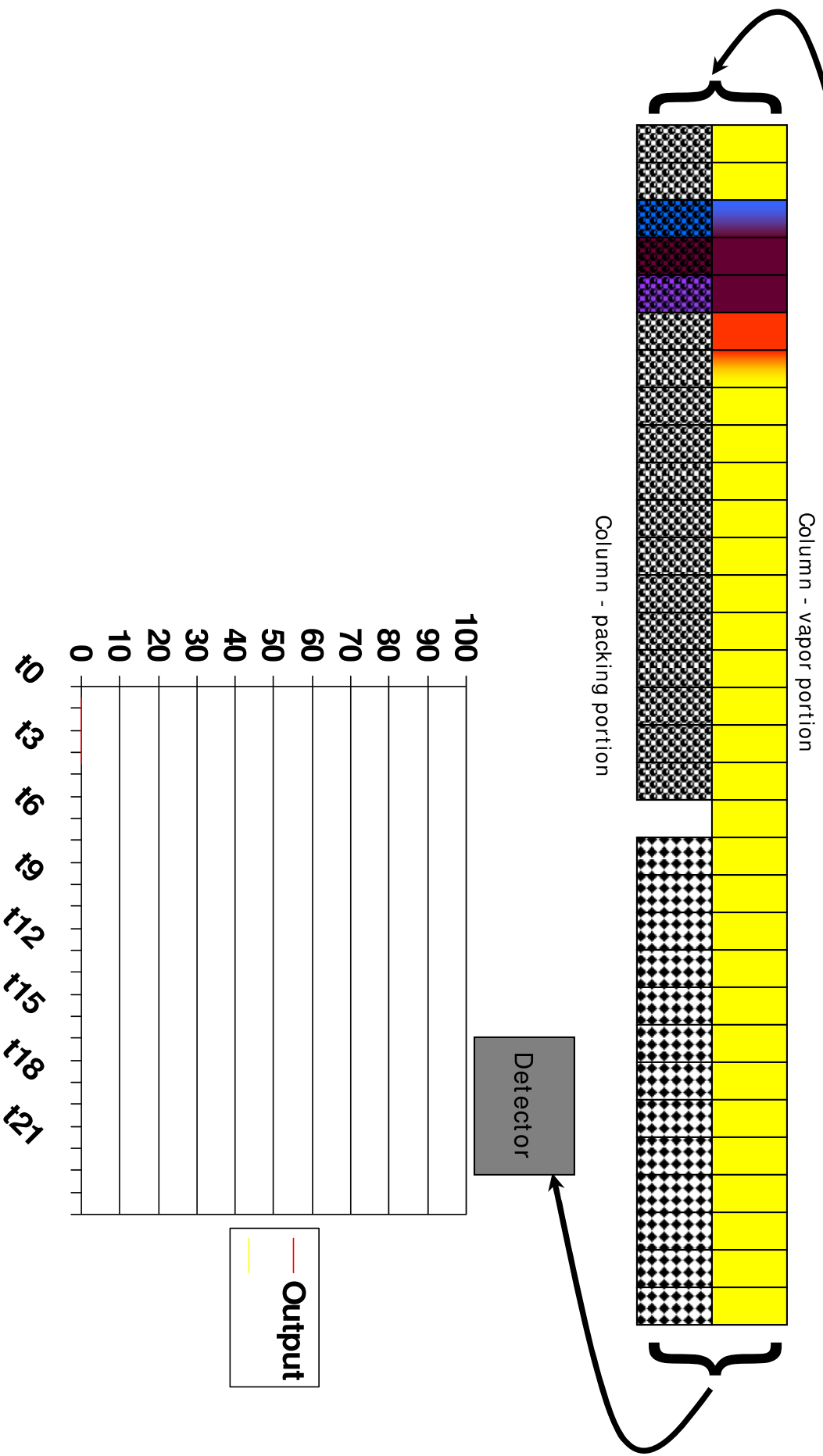
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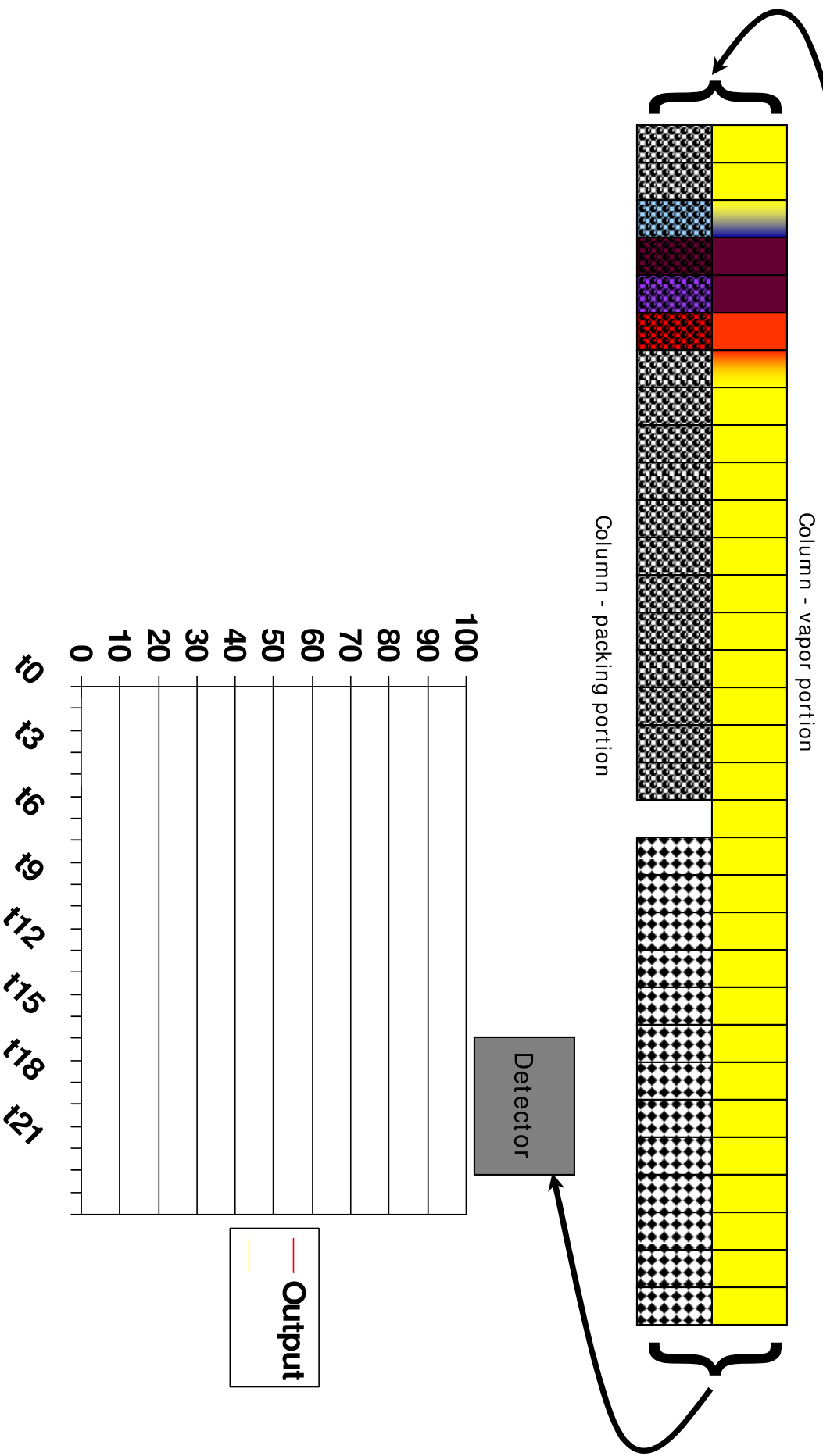
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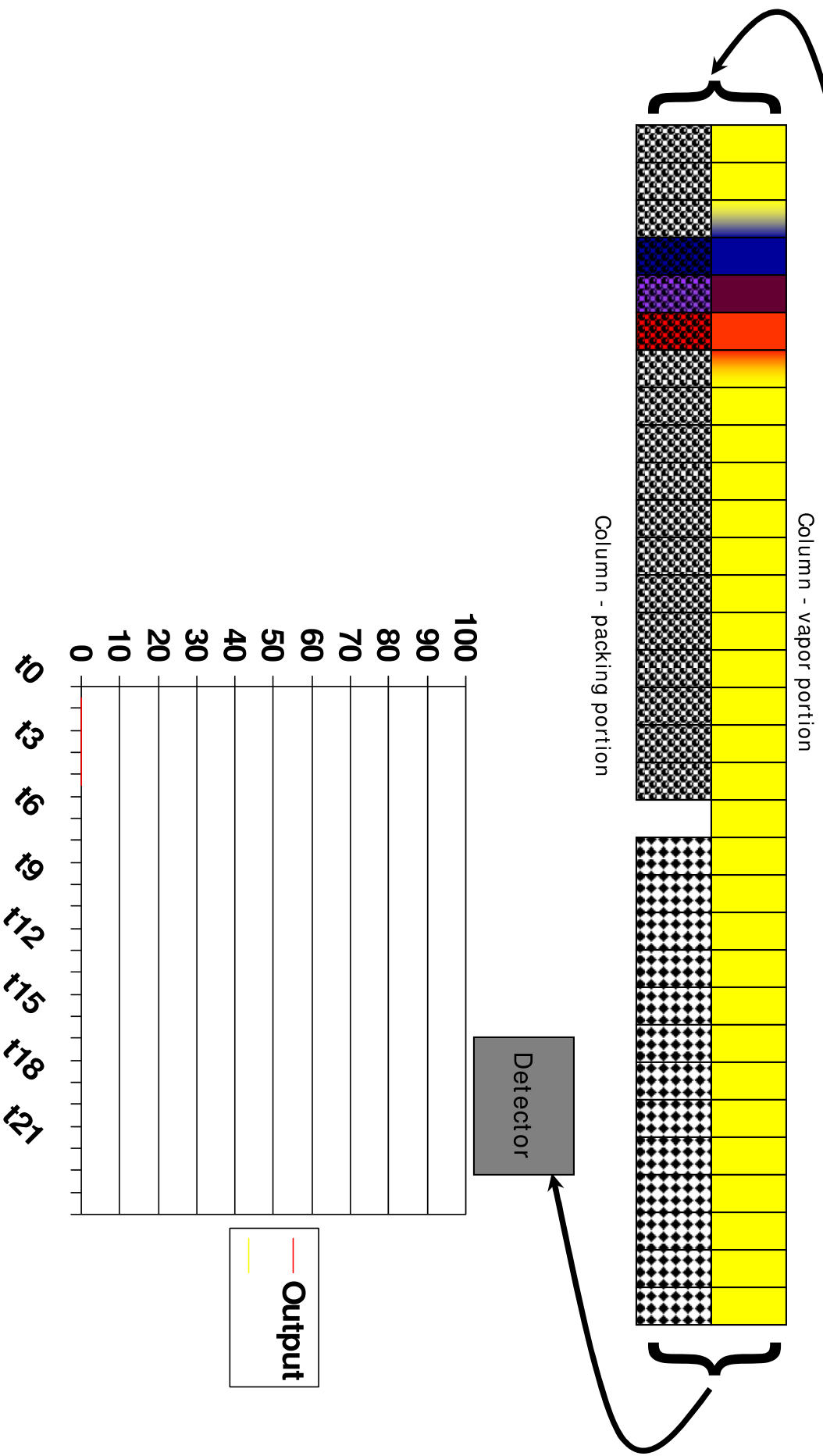
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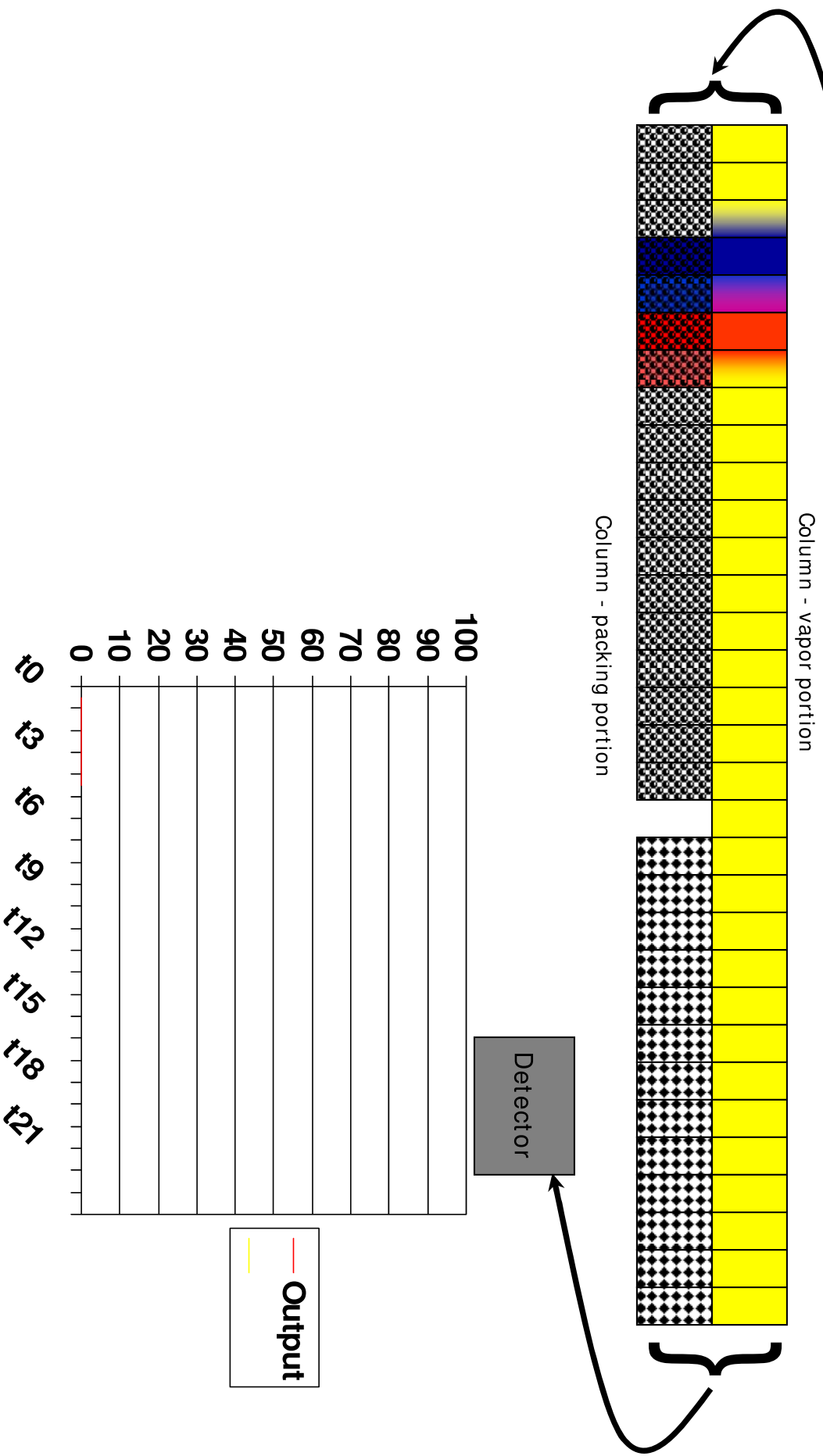
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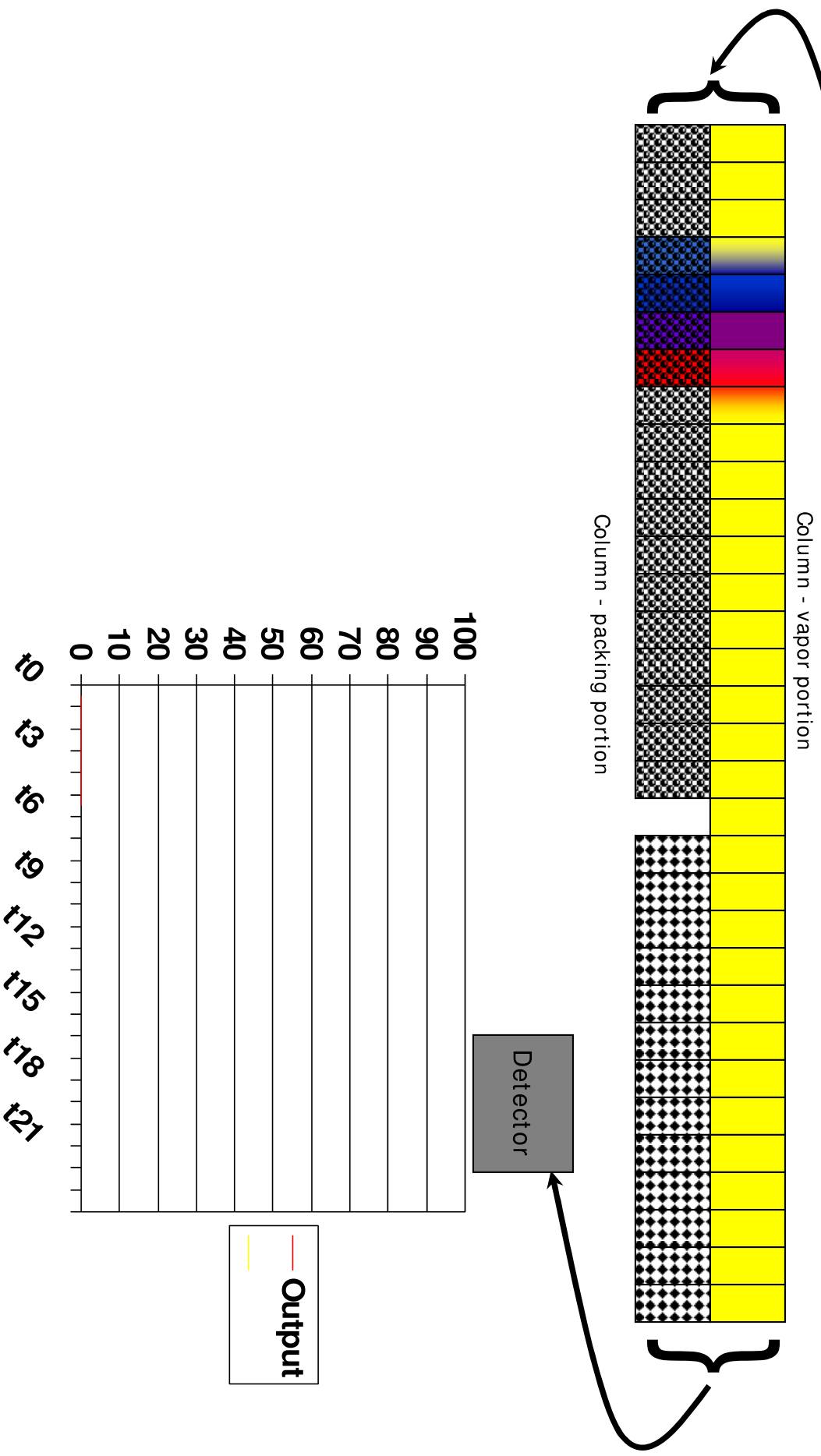
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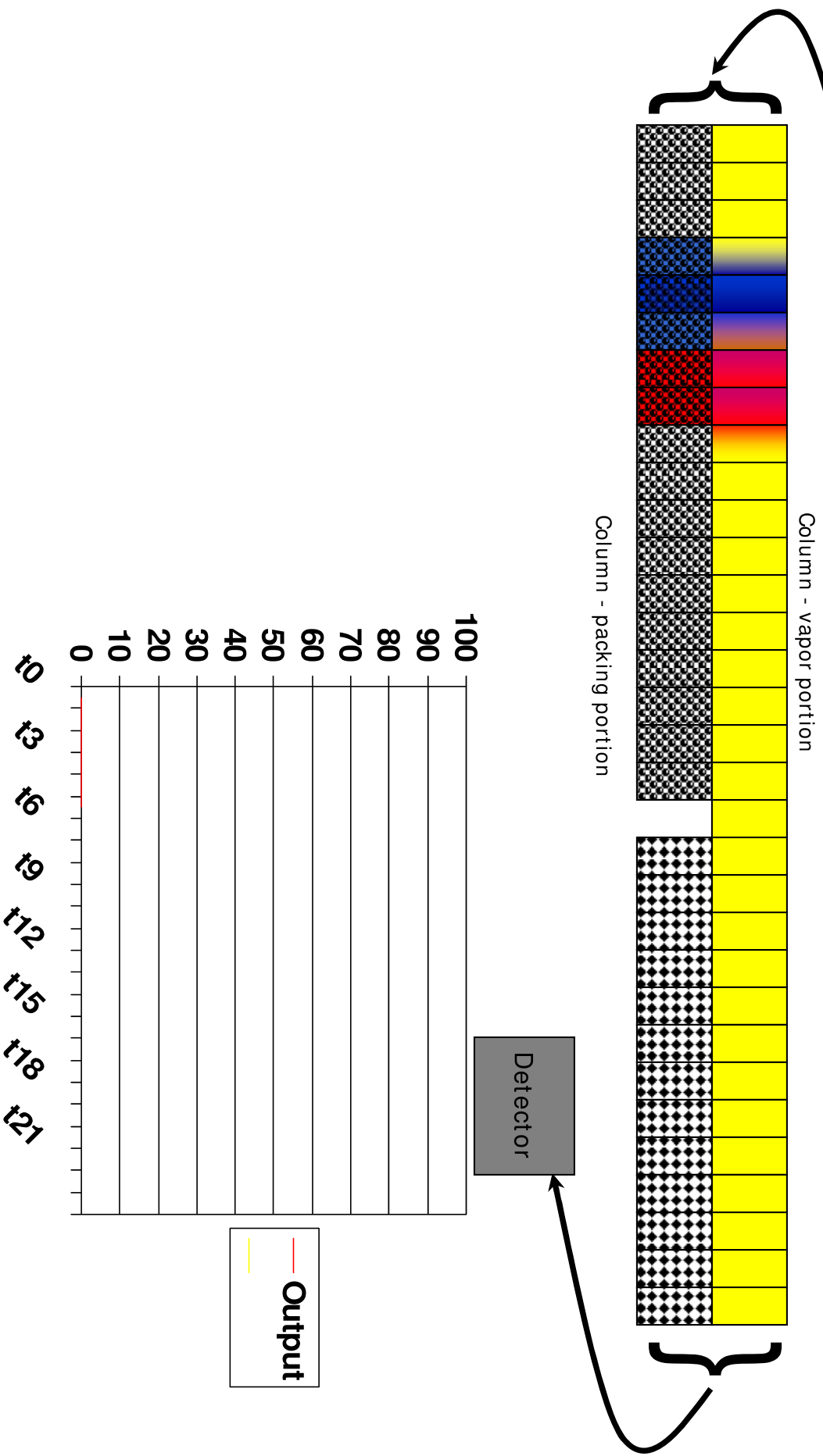
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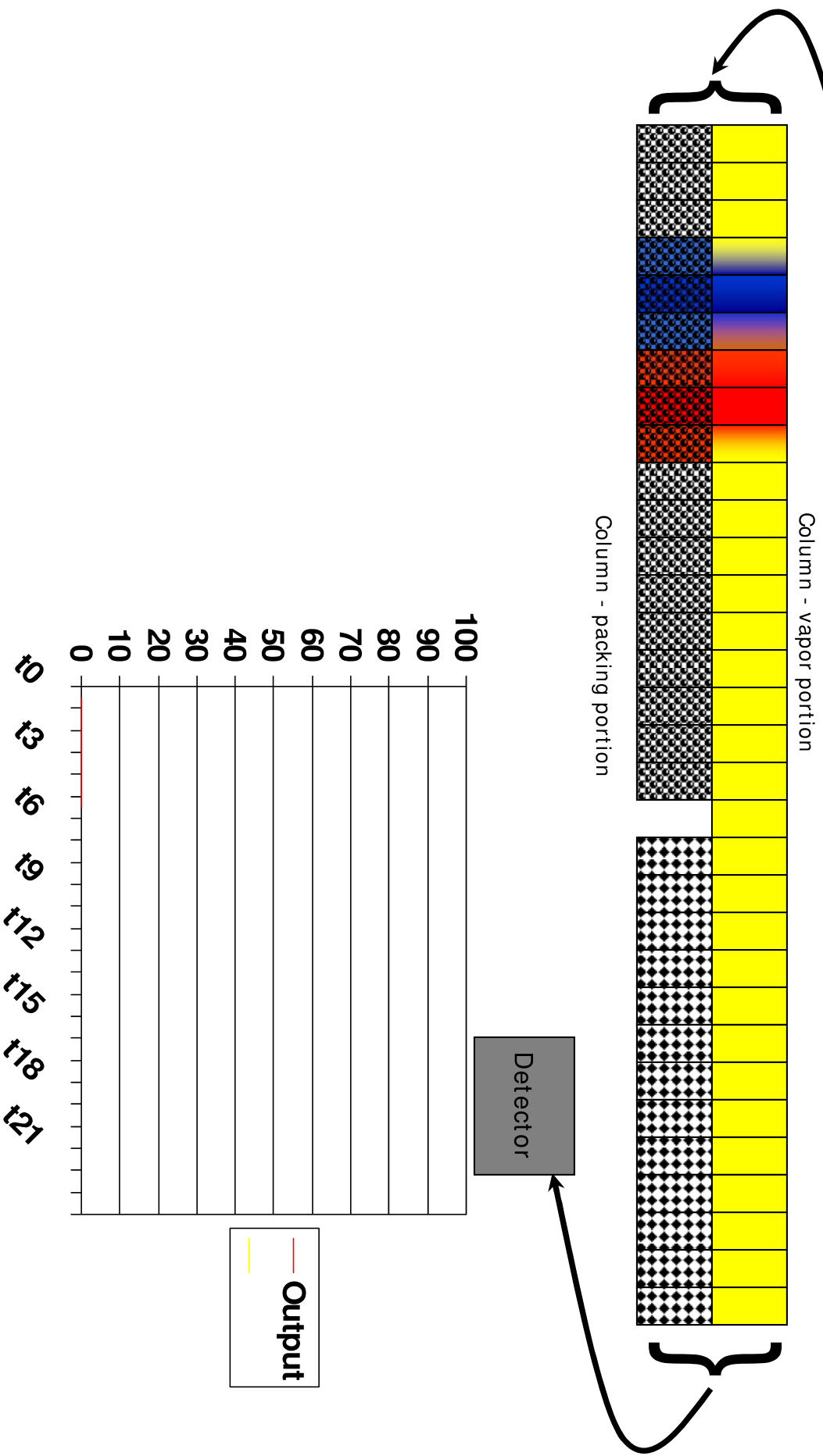
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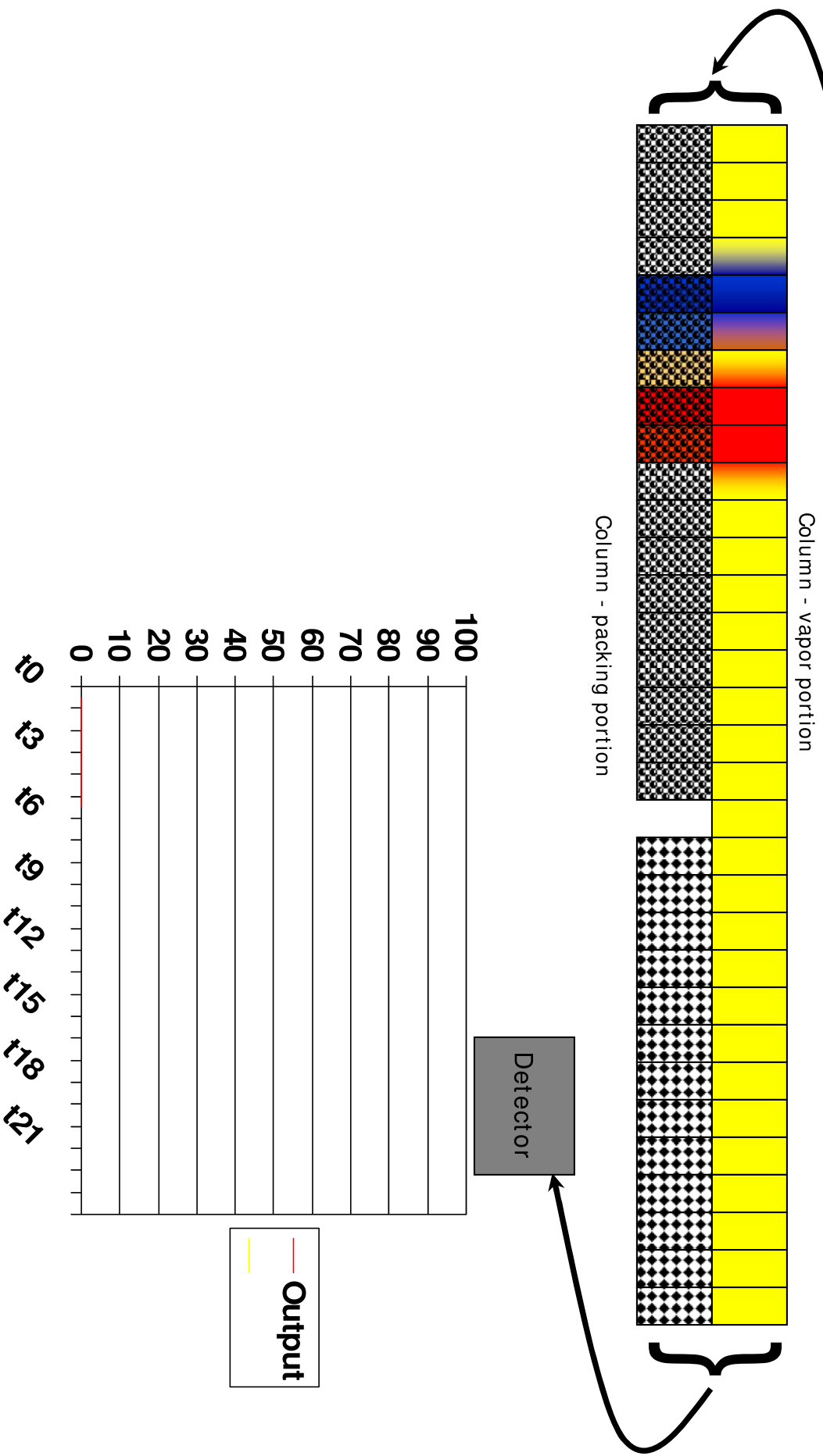
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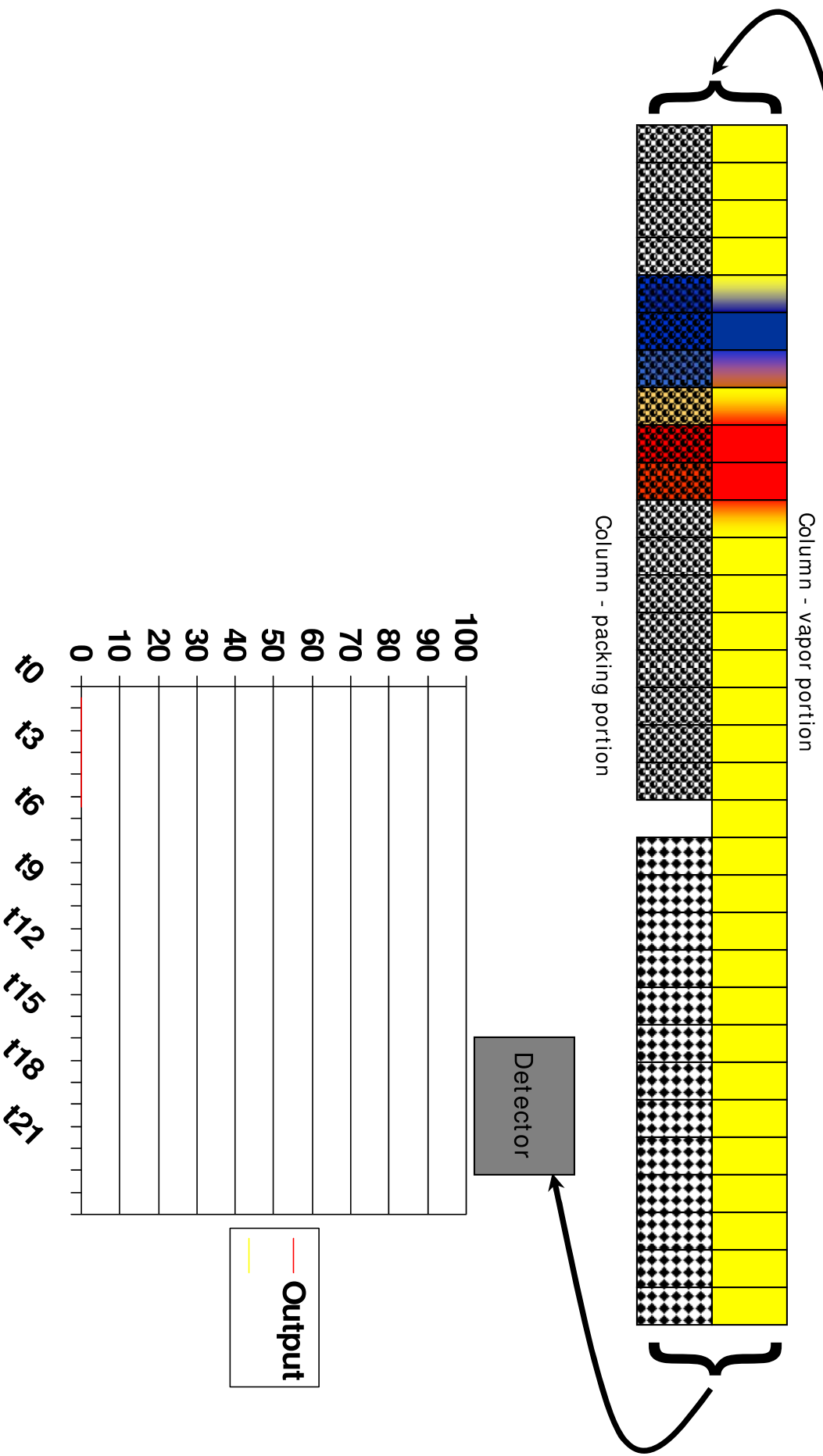
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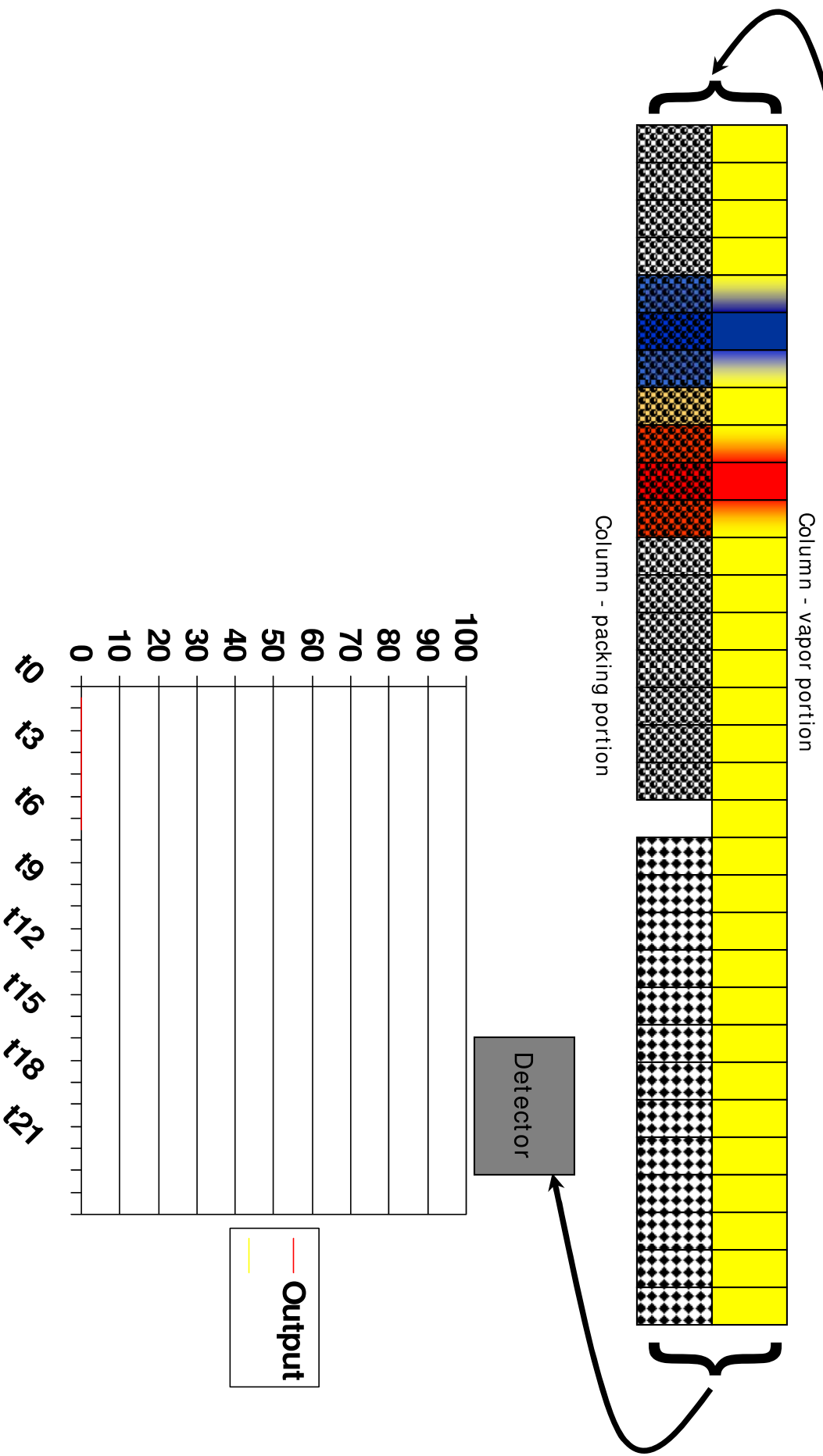
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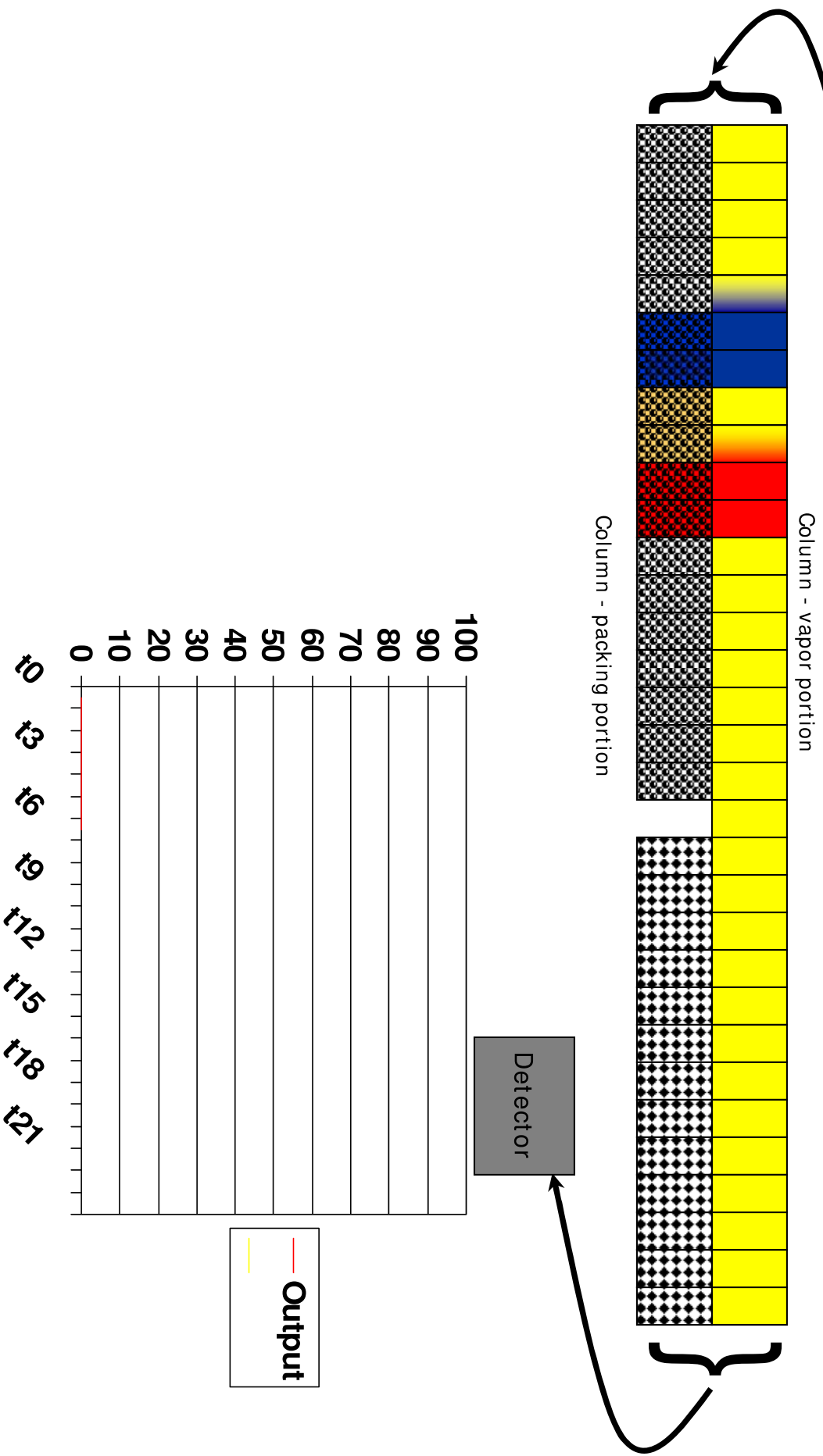
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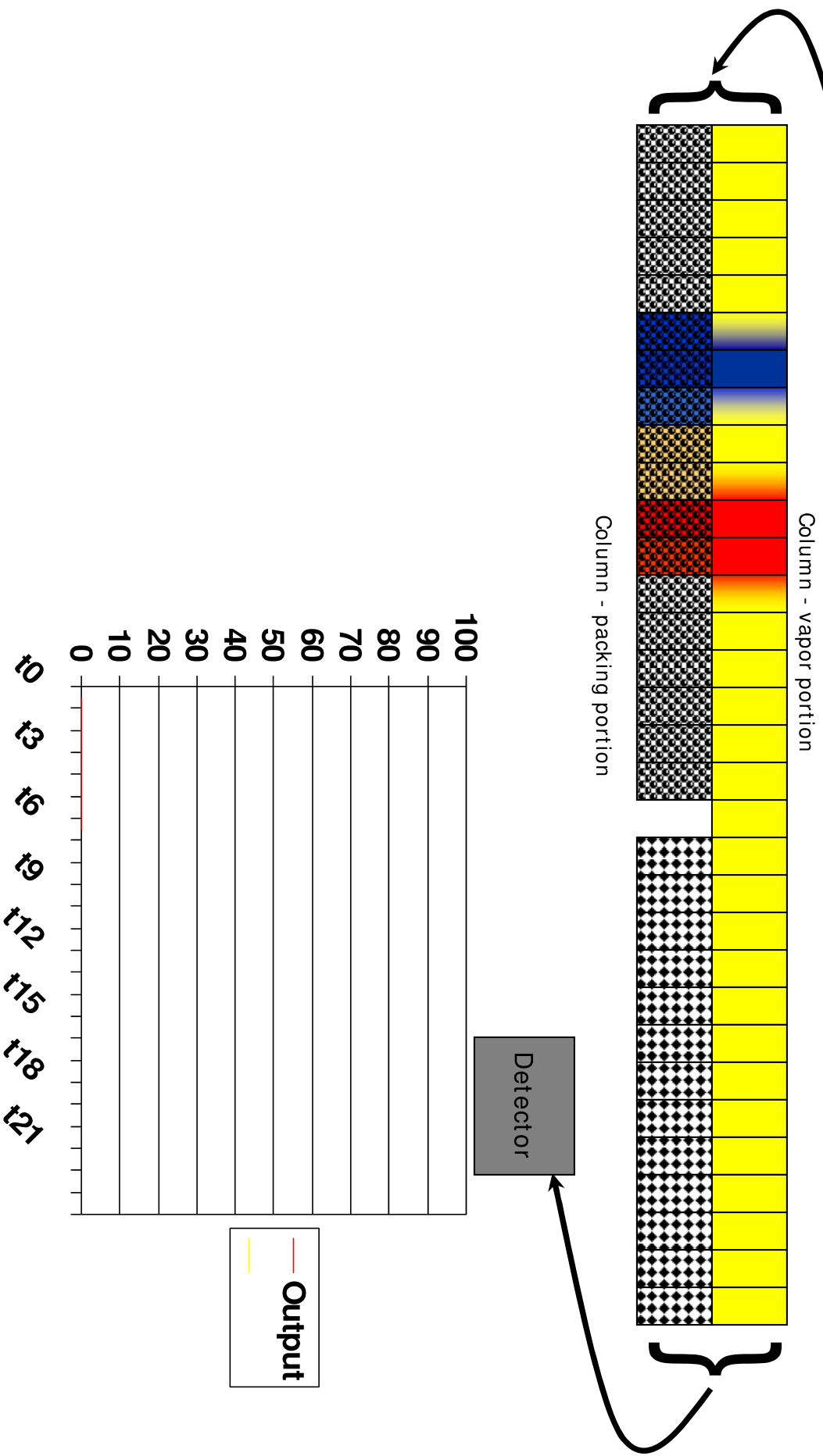
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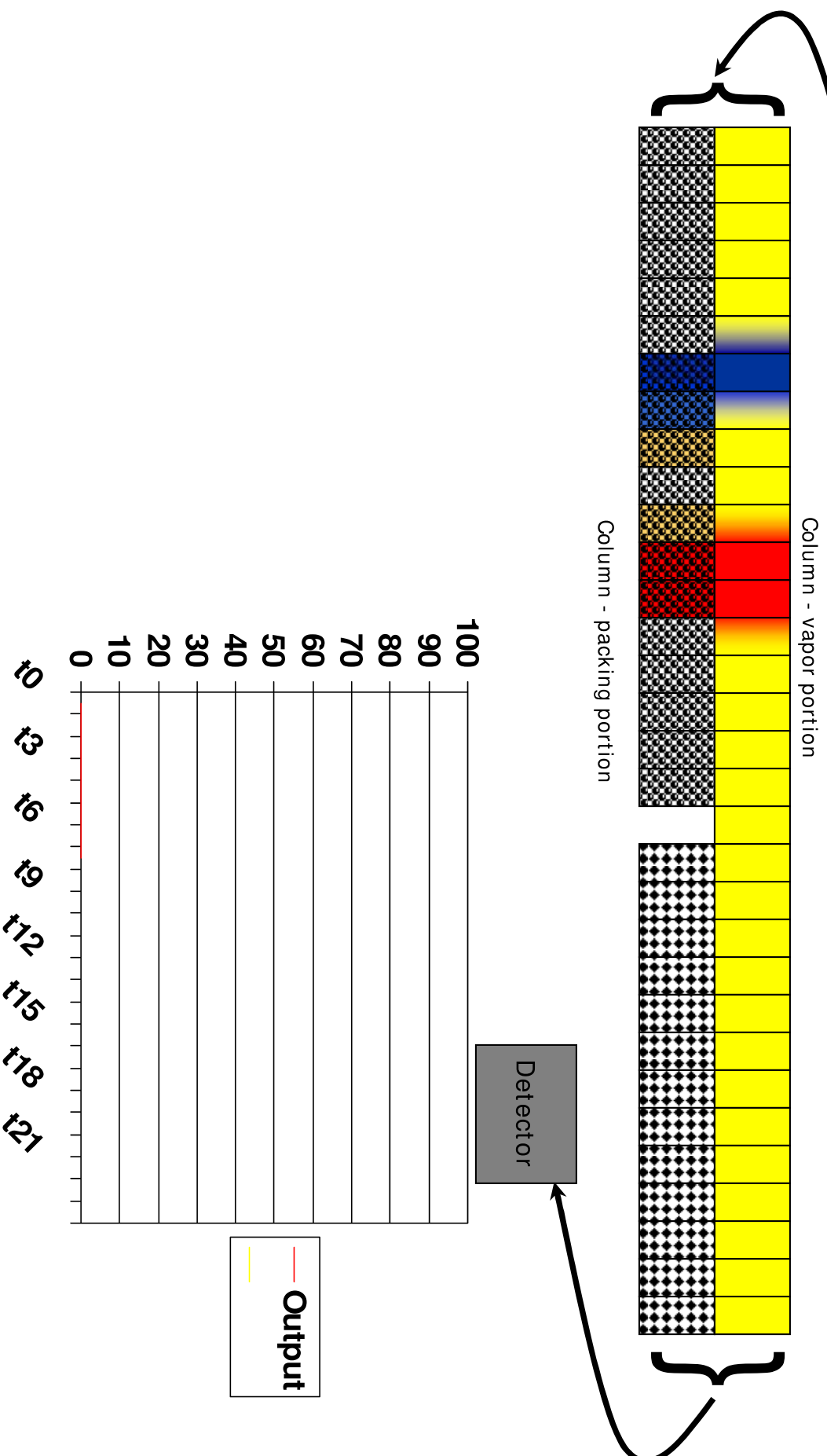
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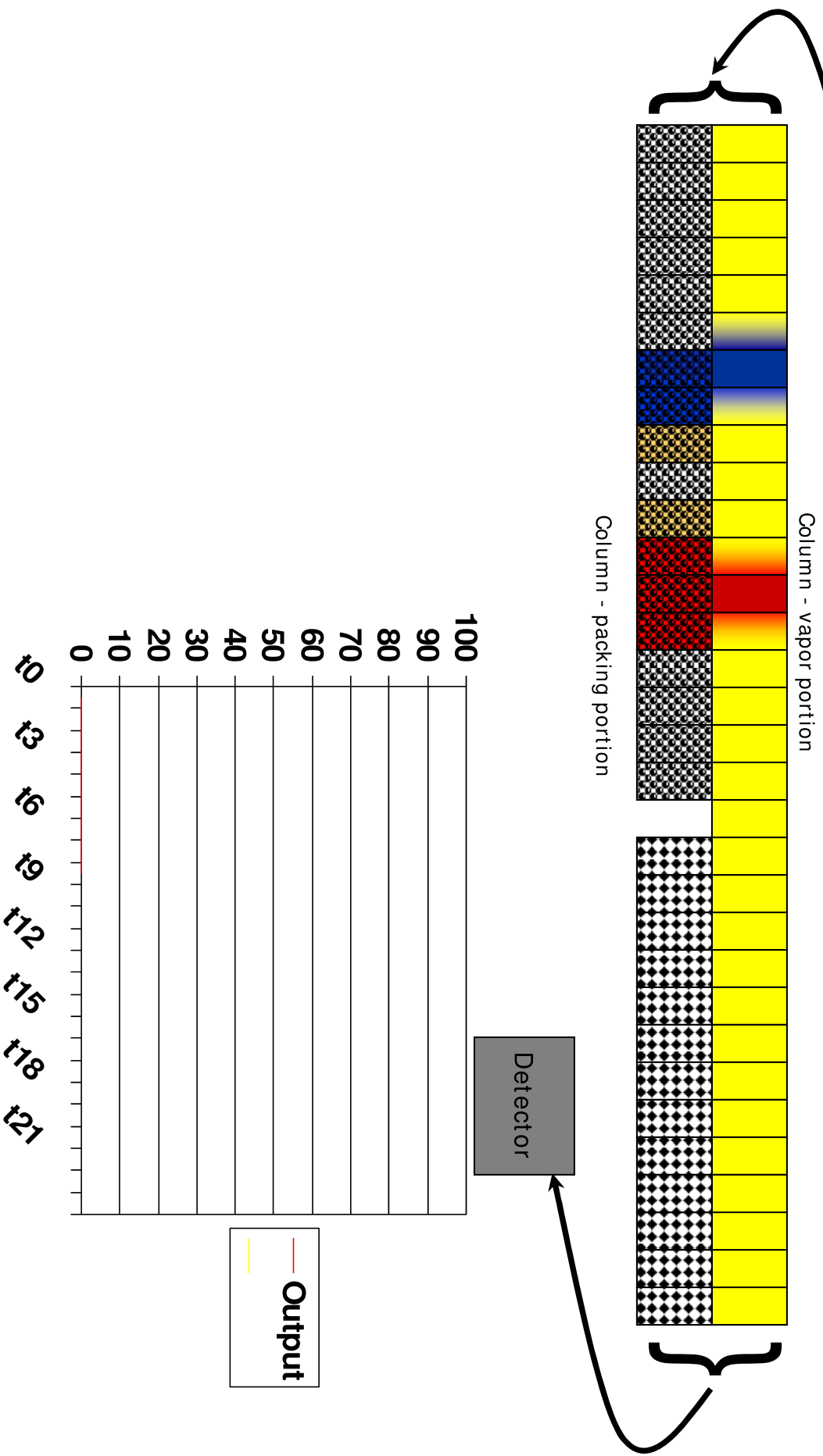
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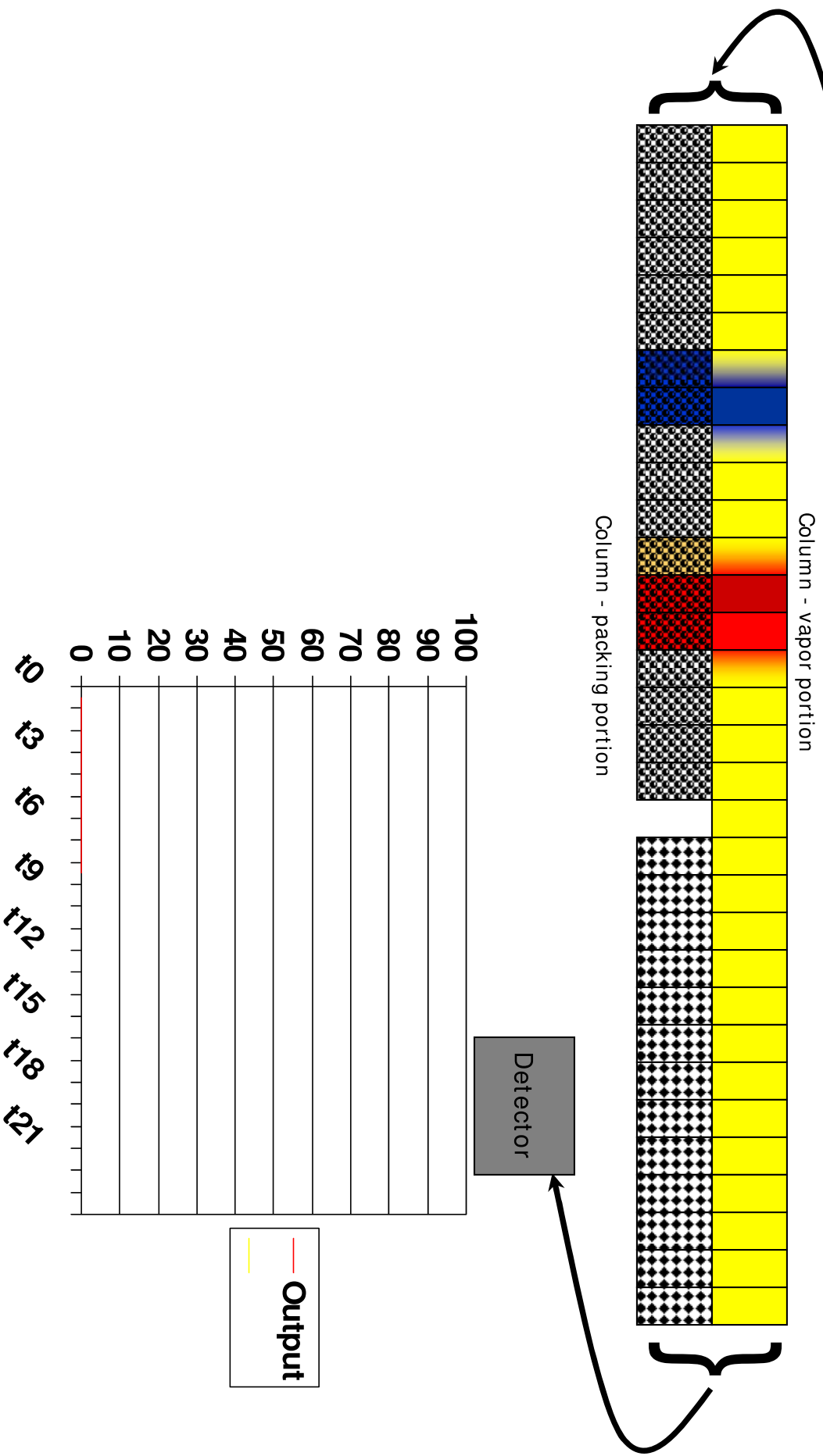
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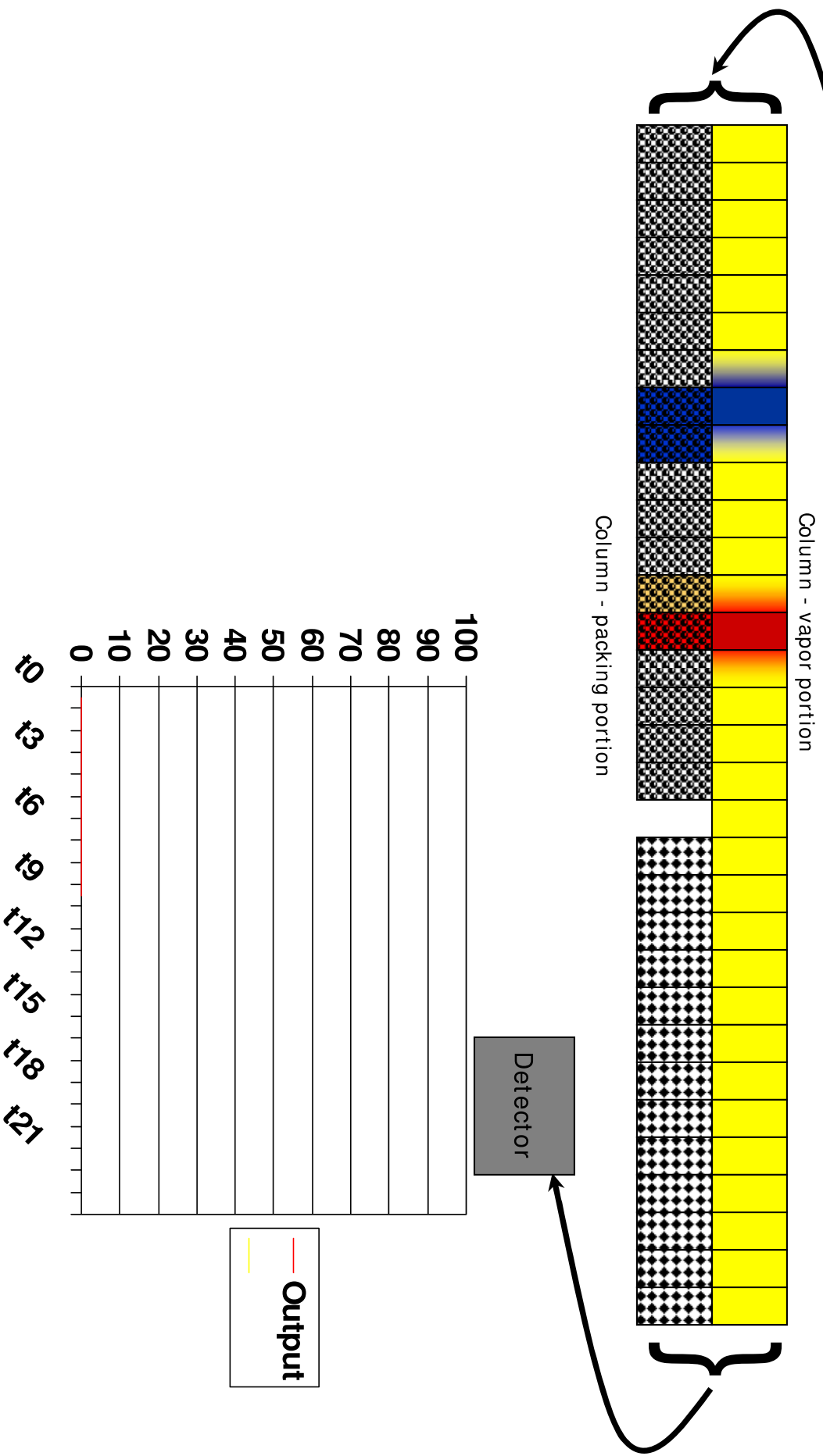
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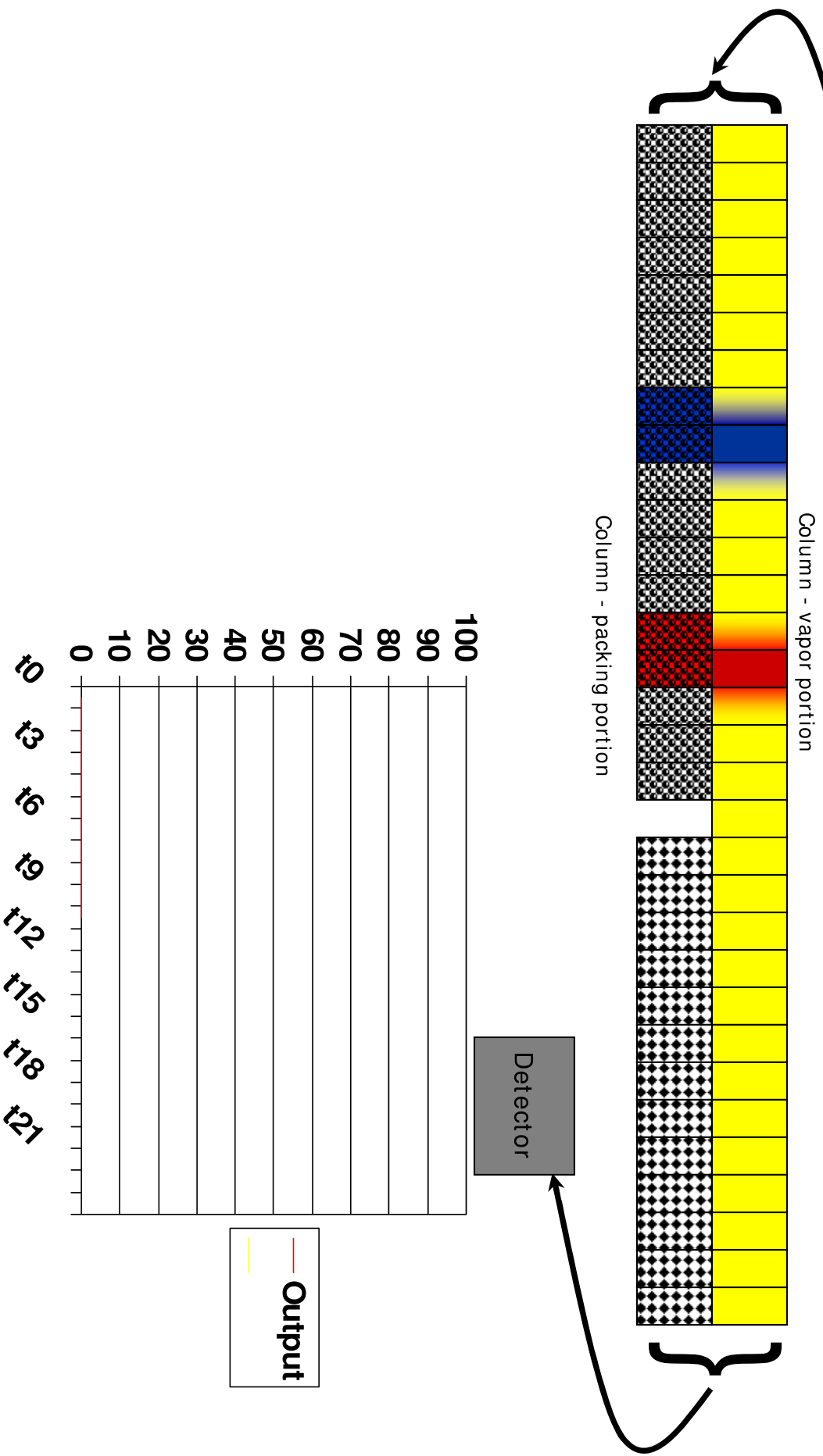
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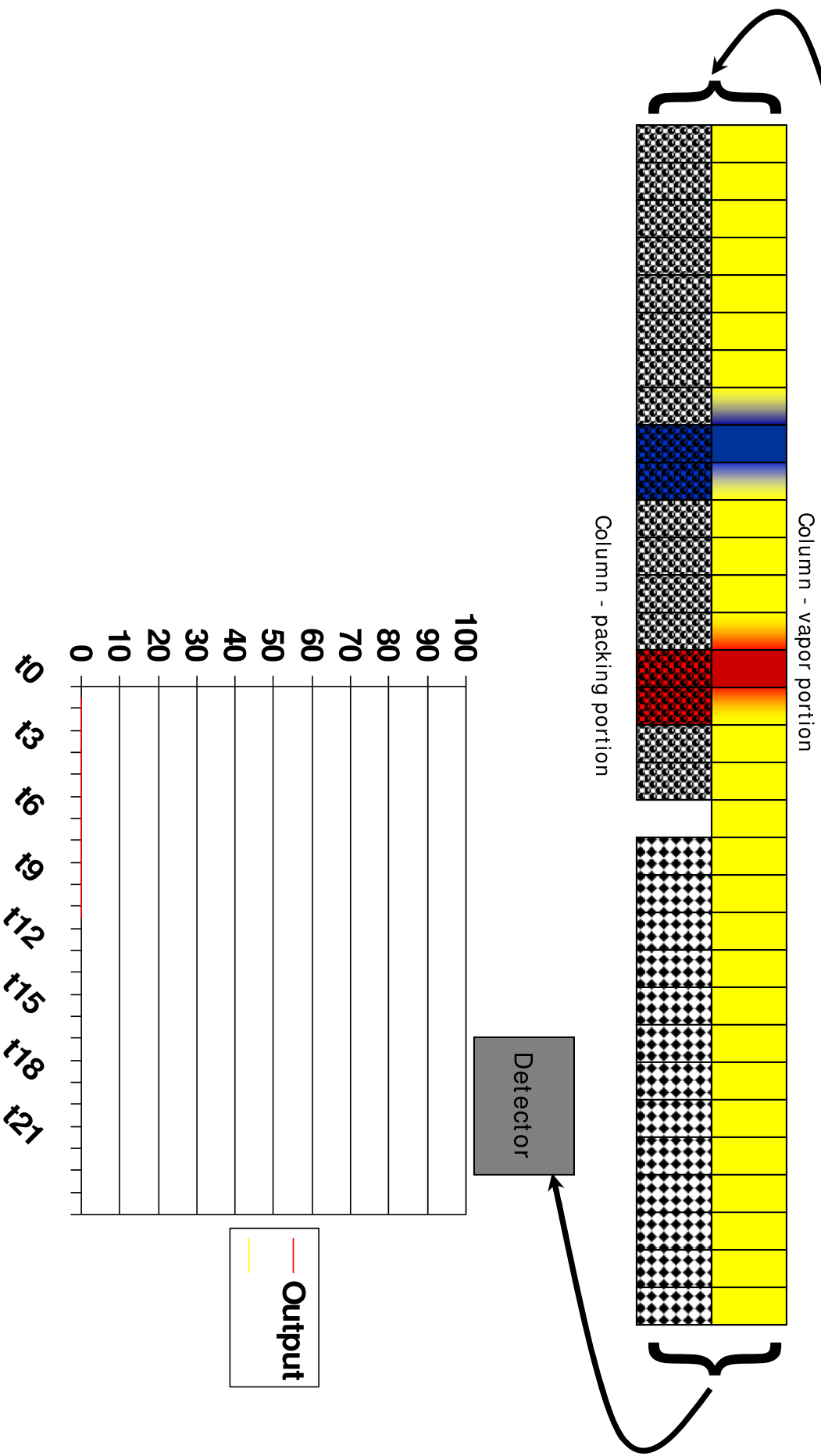
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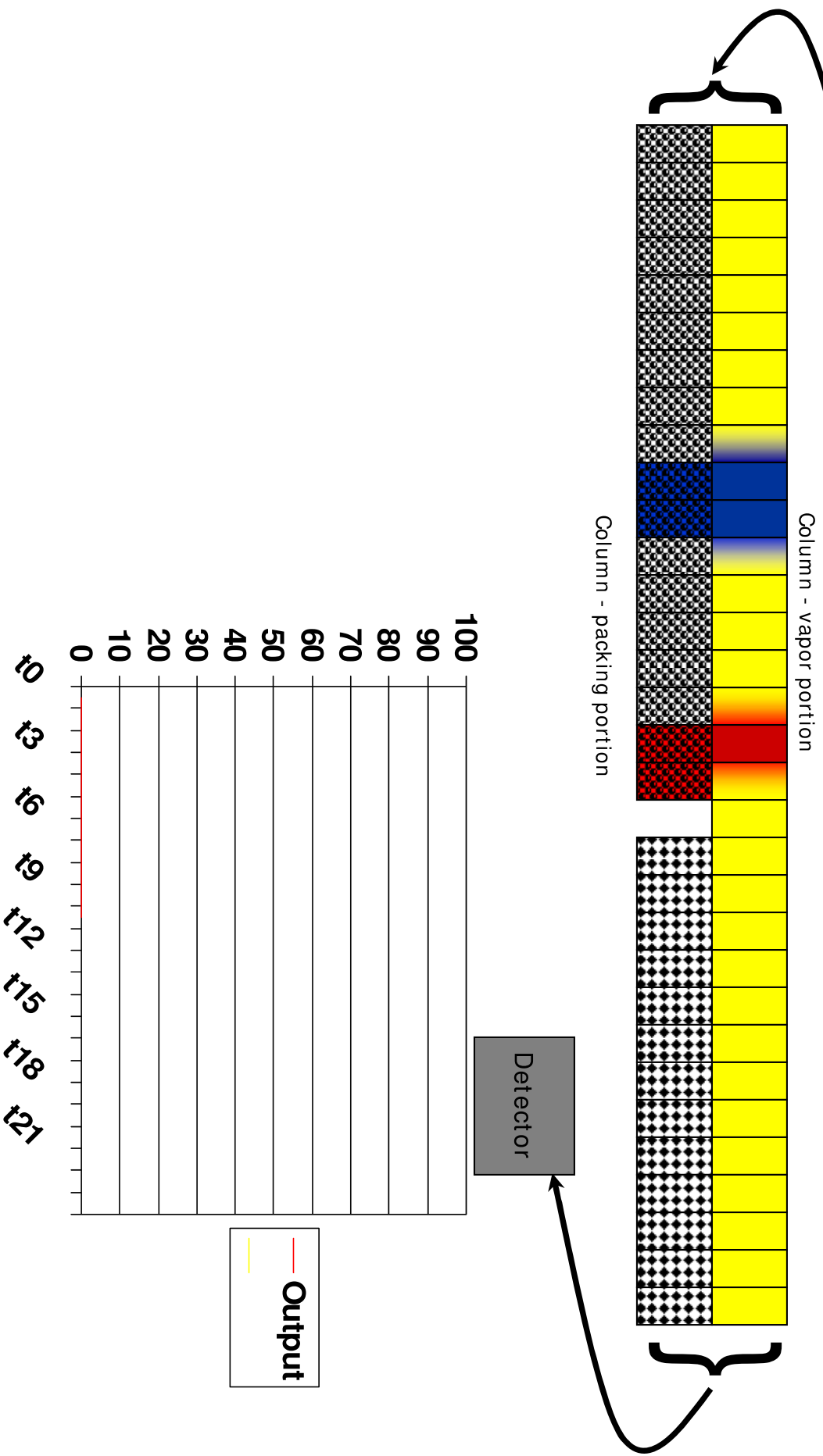
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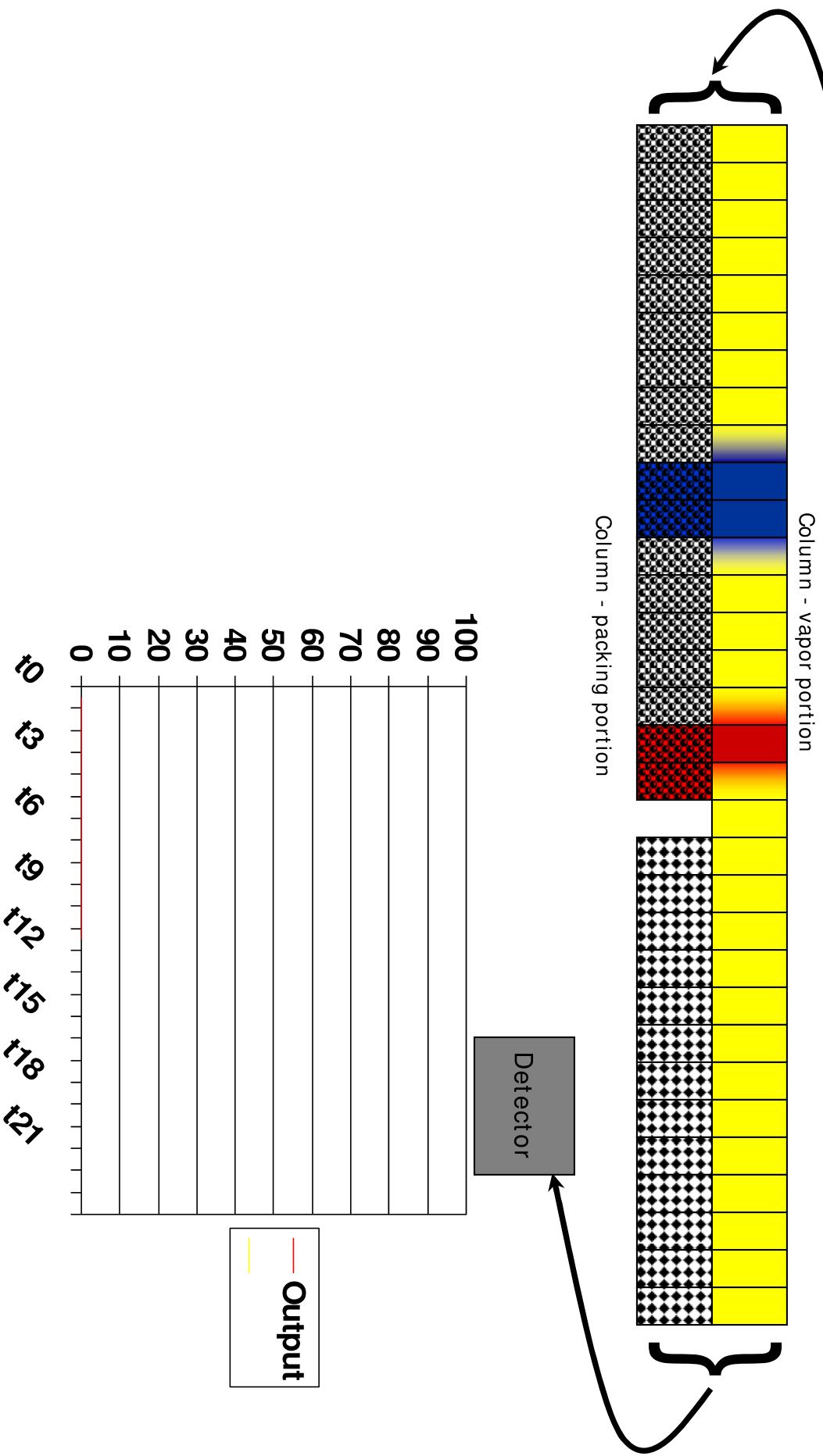
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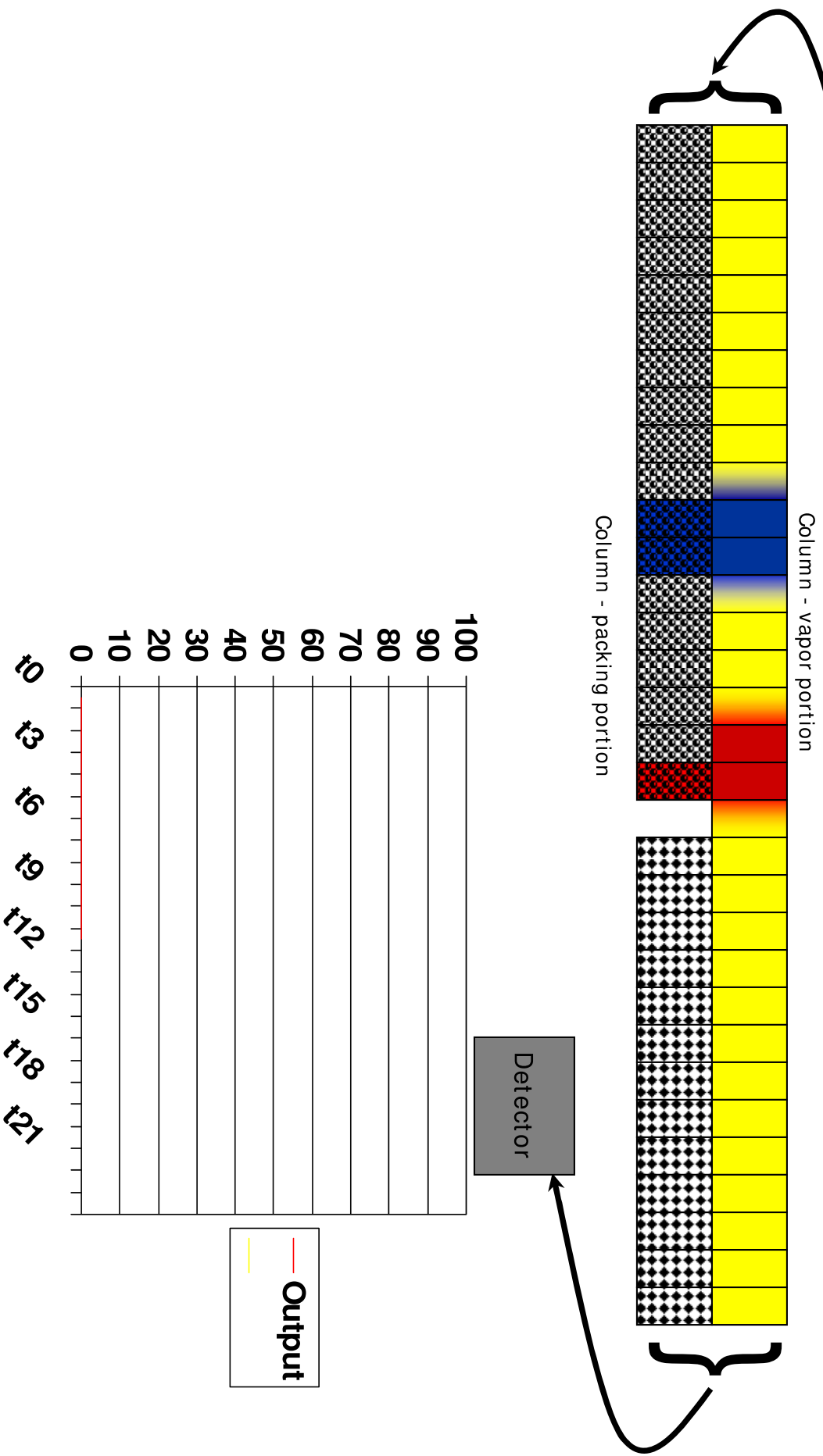
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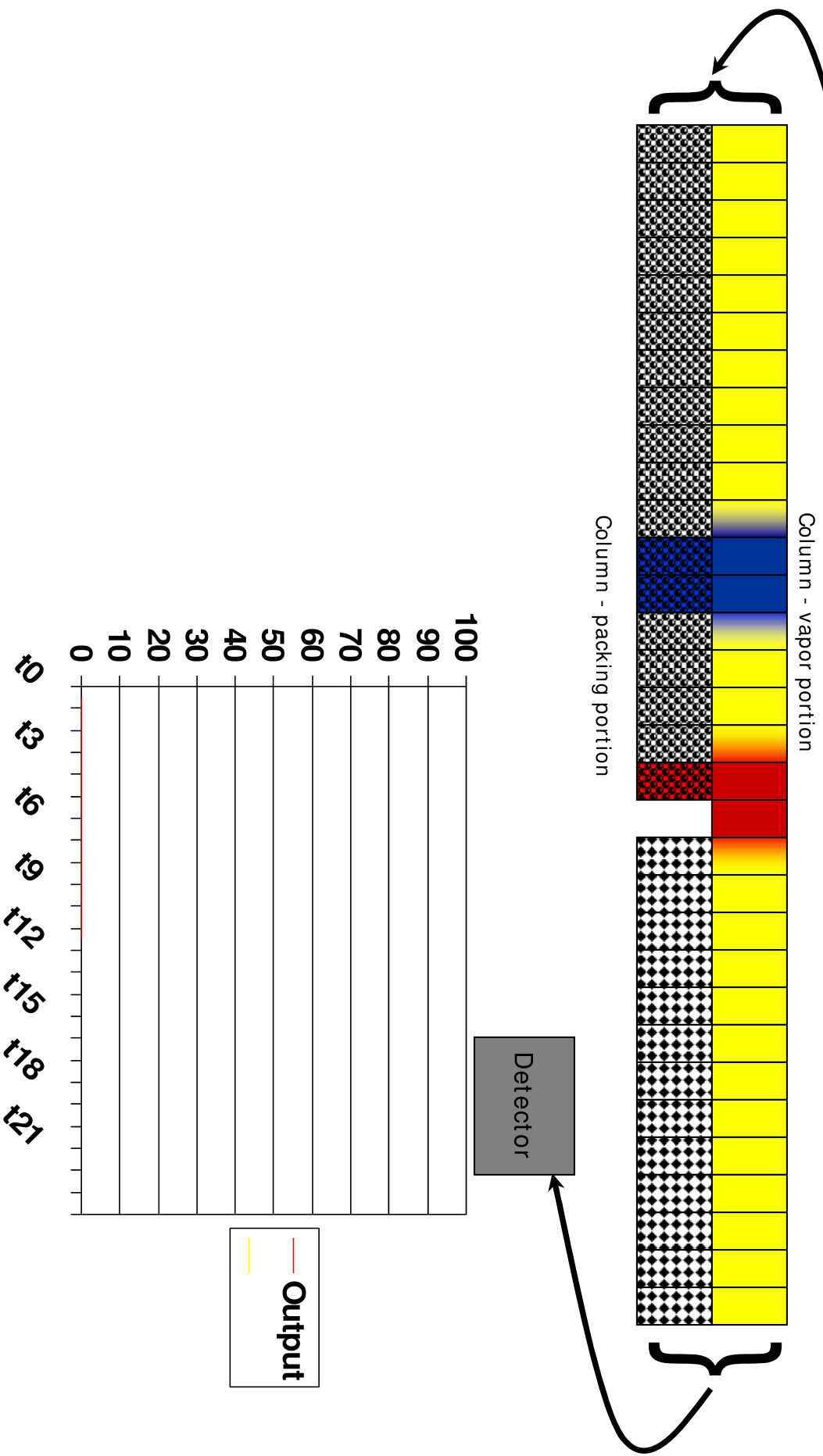
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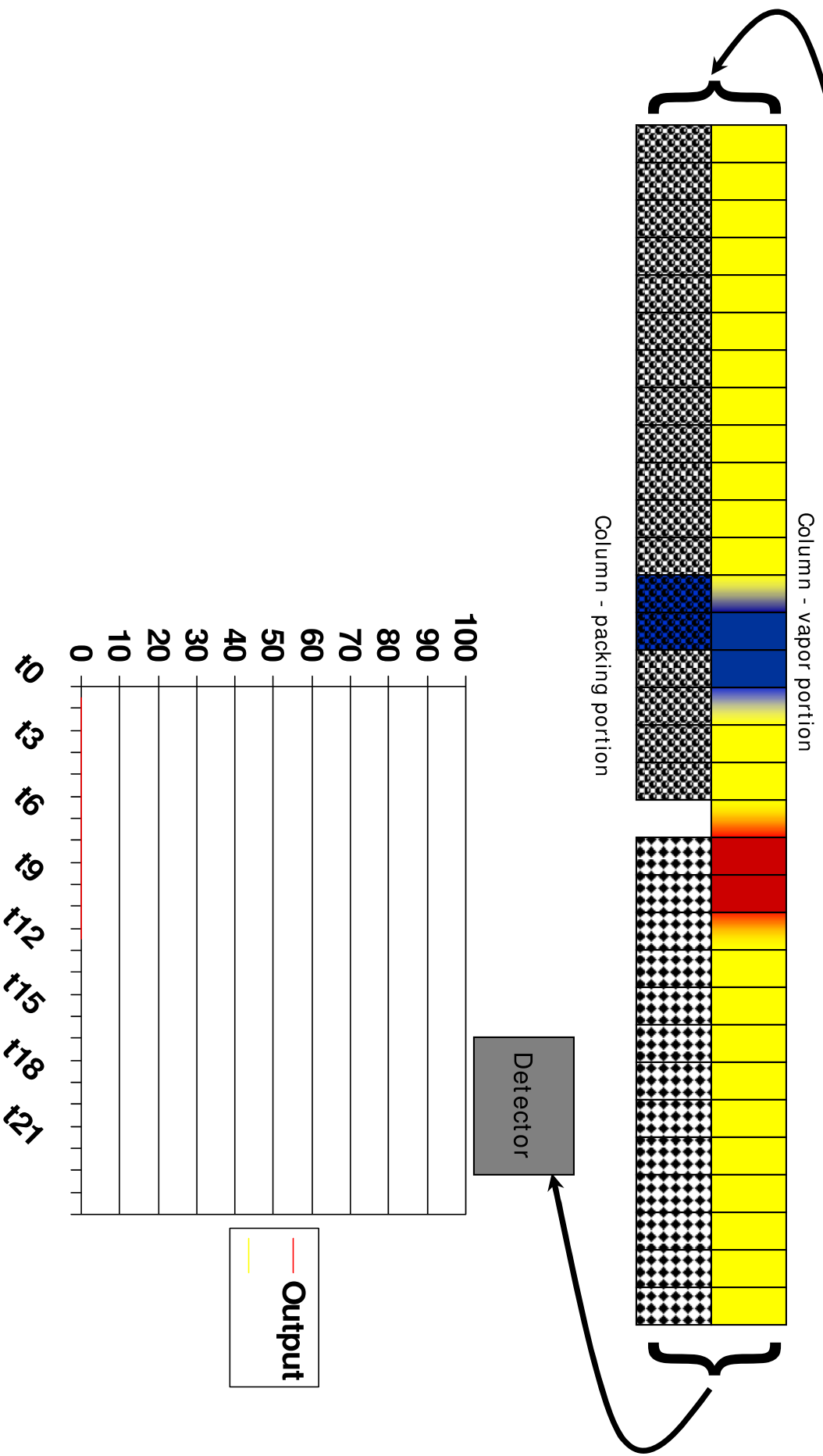
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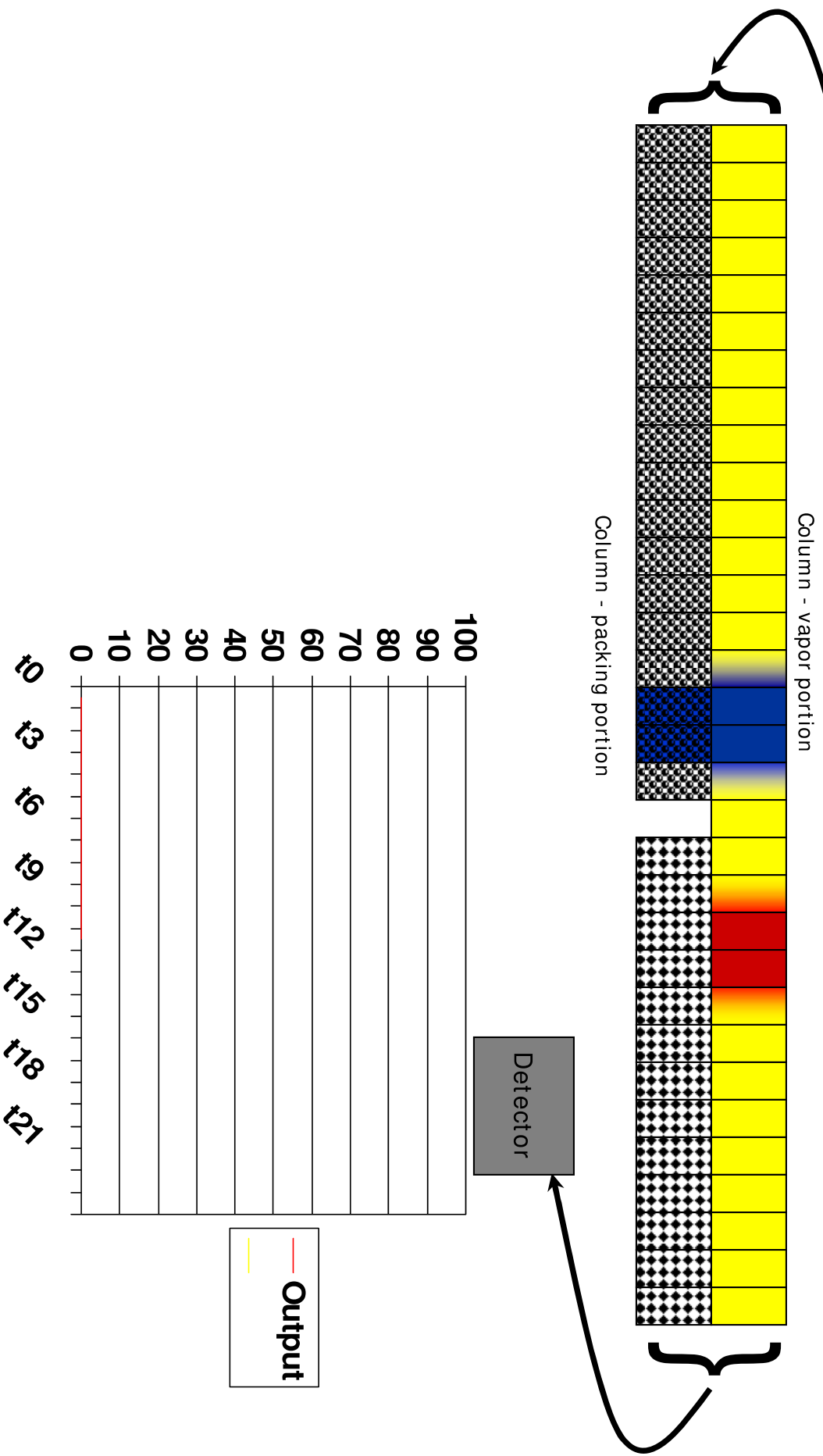
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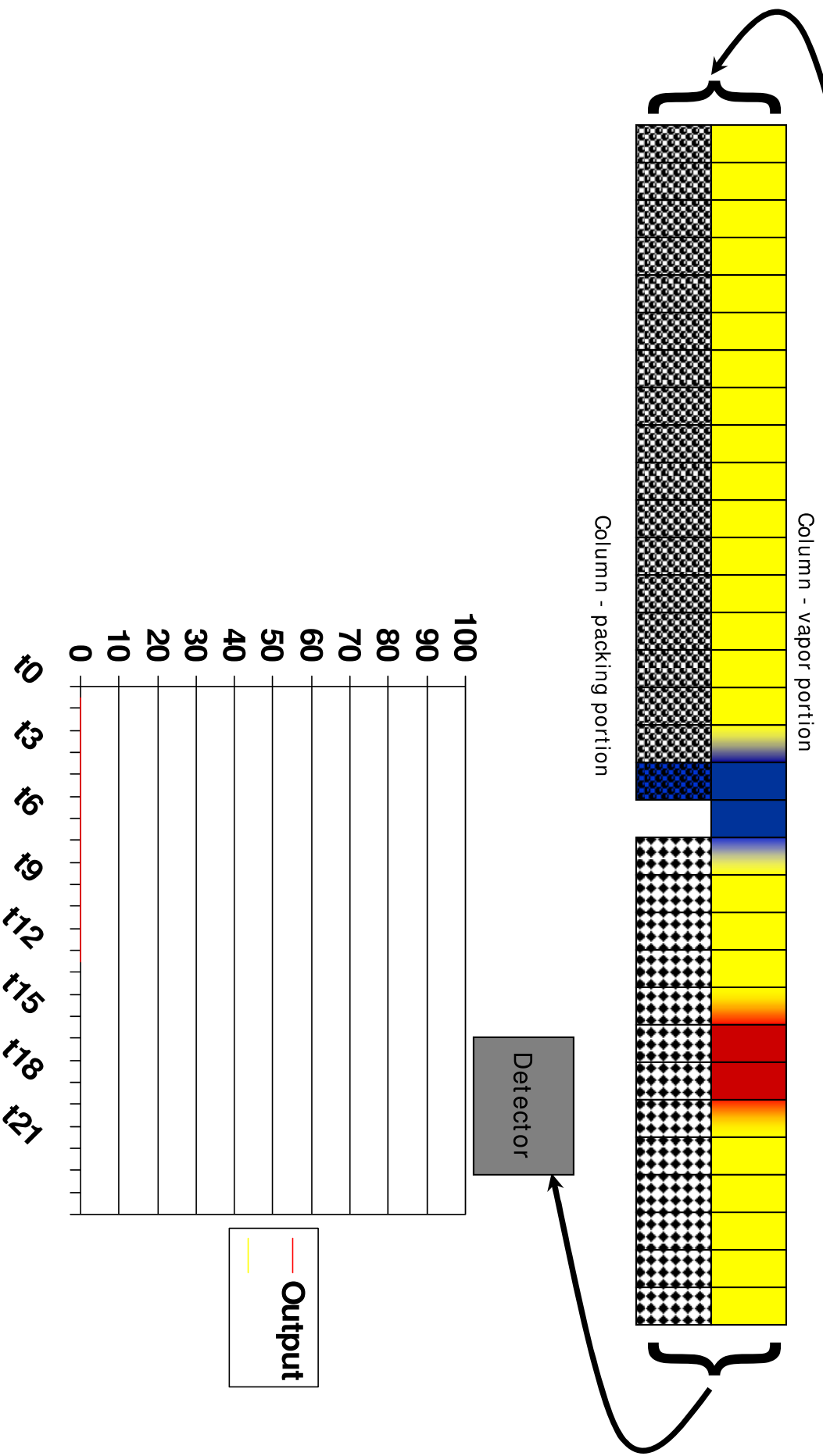
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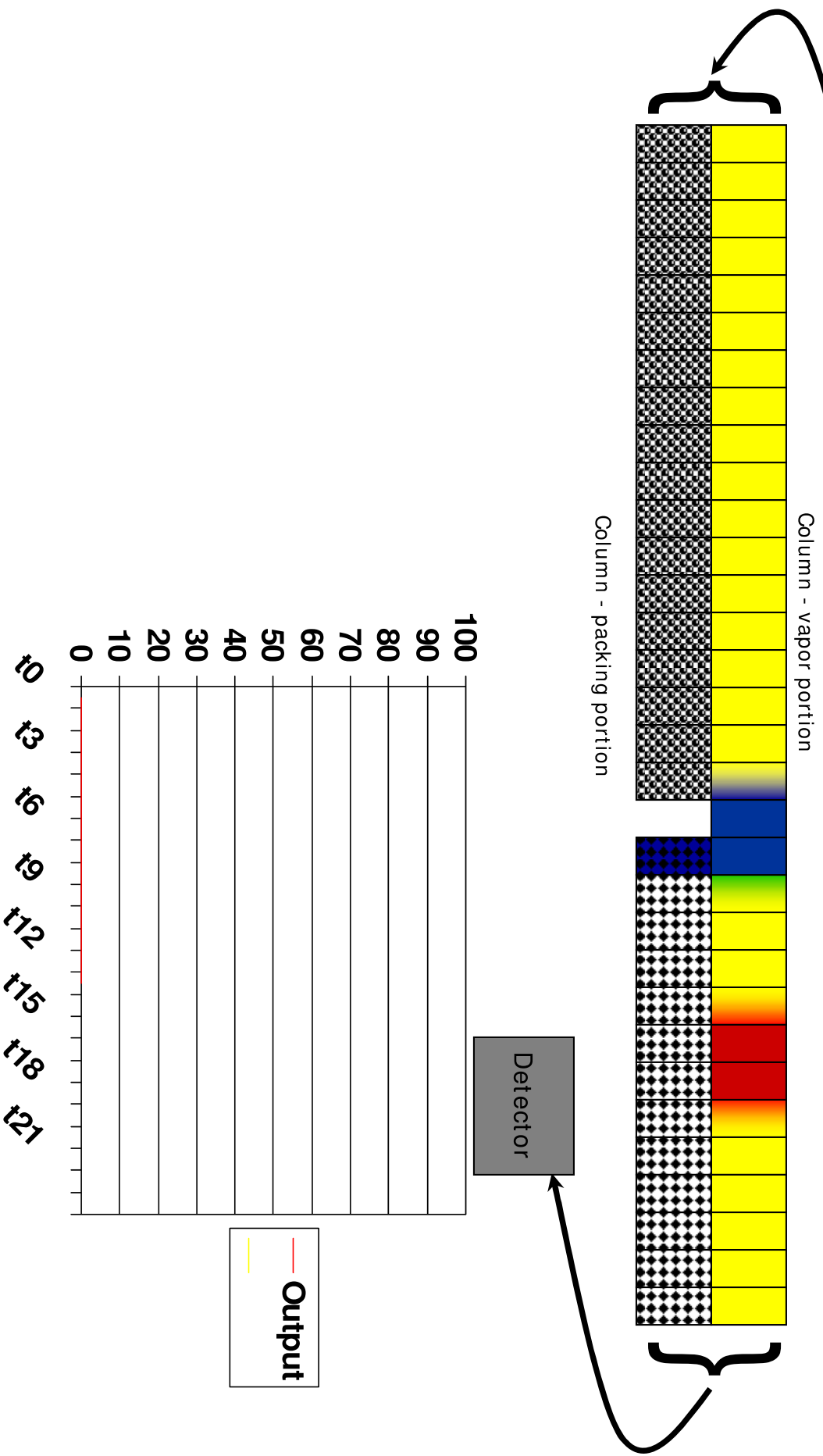
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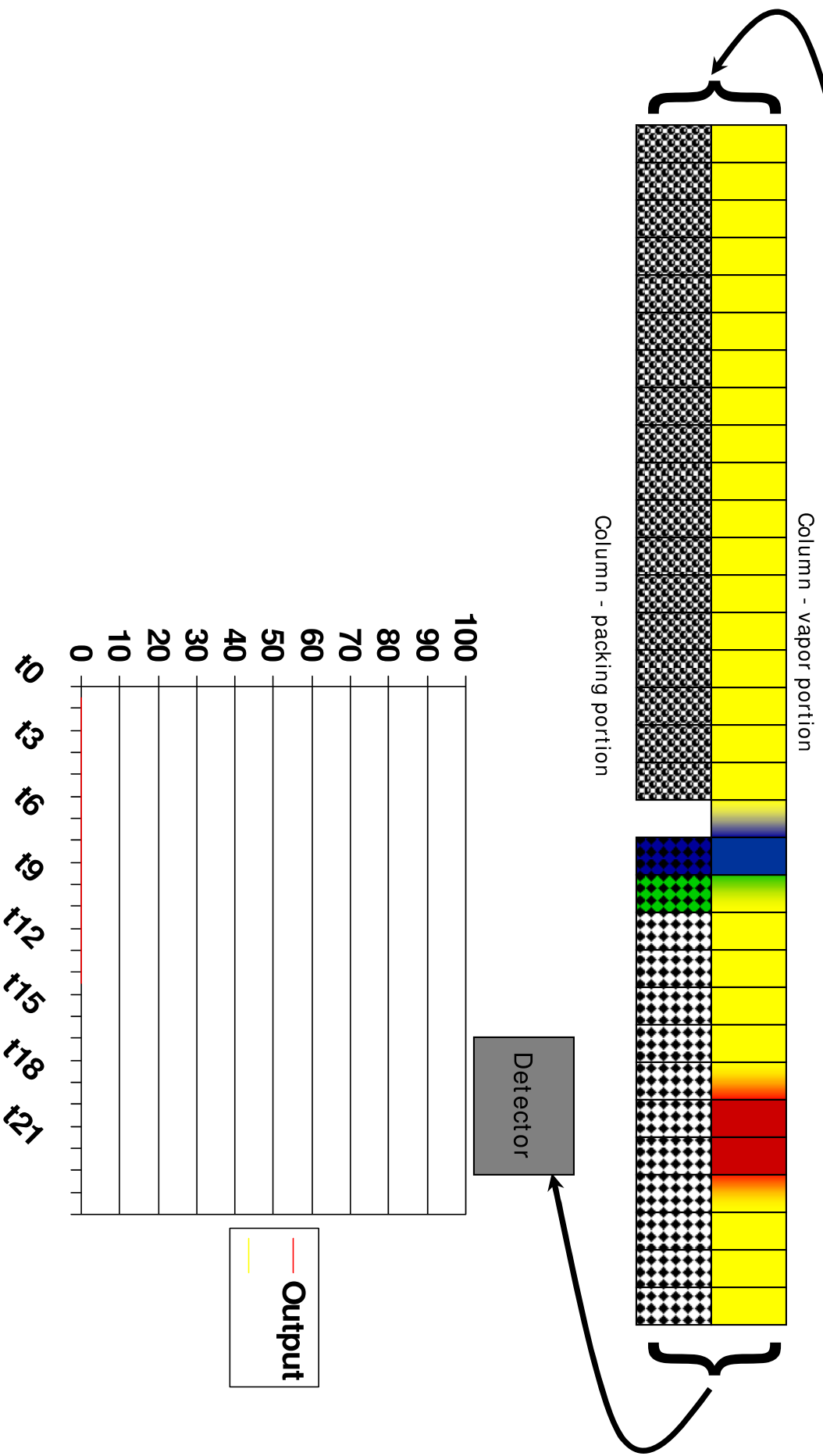
Carrier and sample enter





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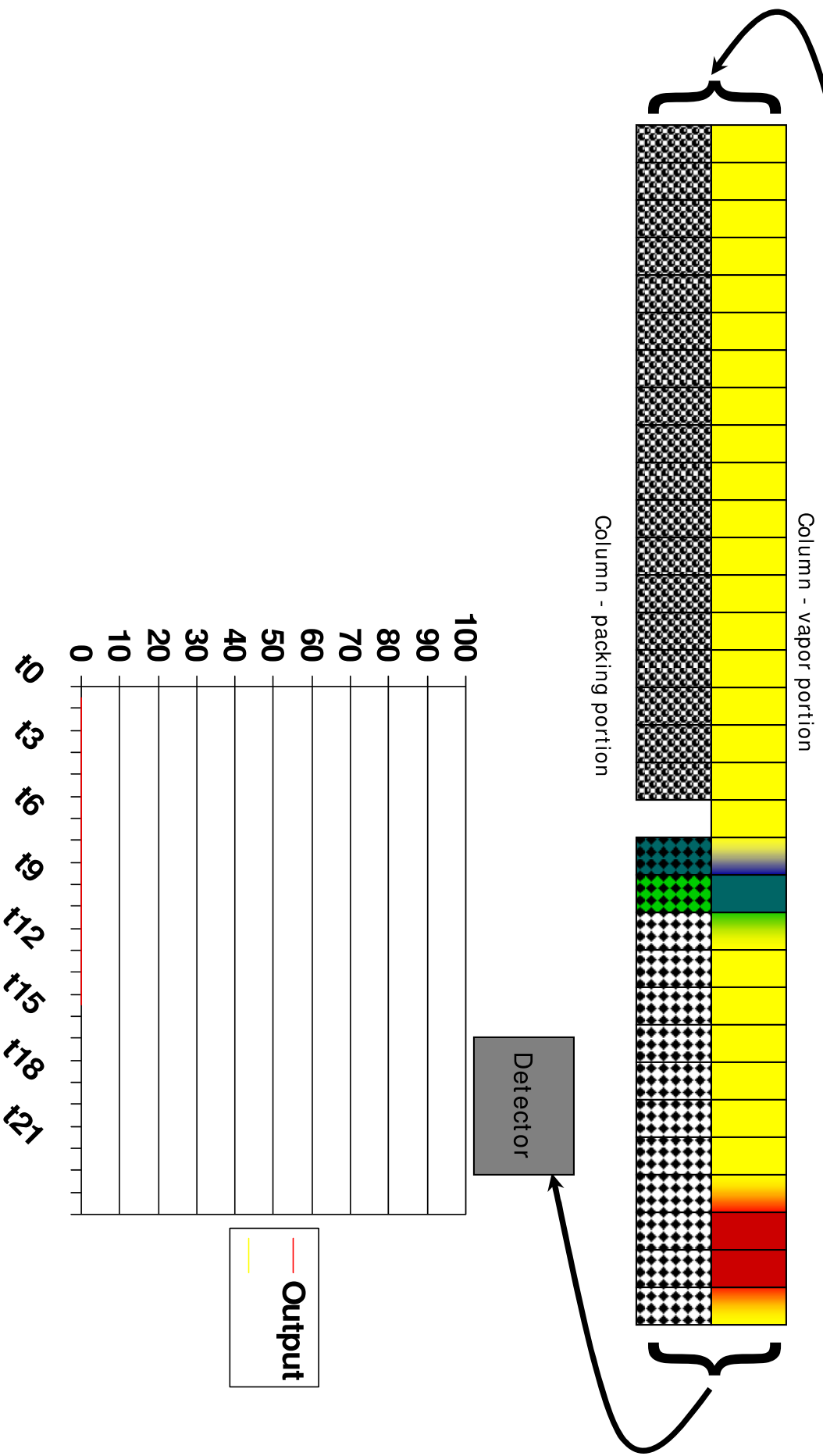
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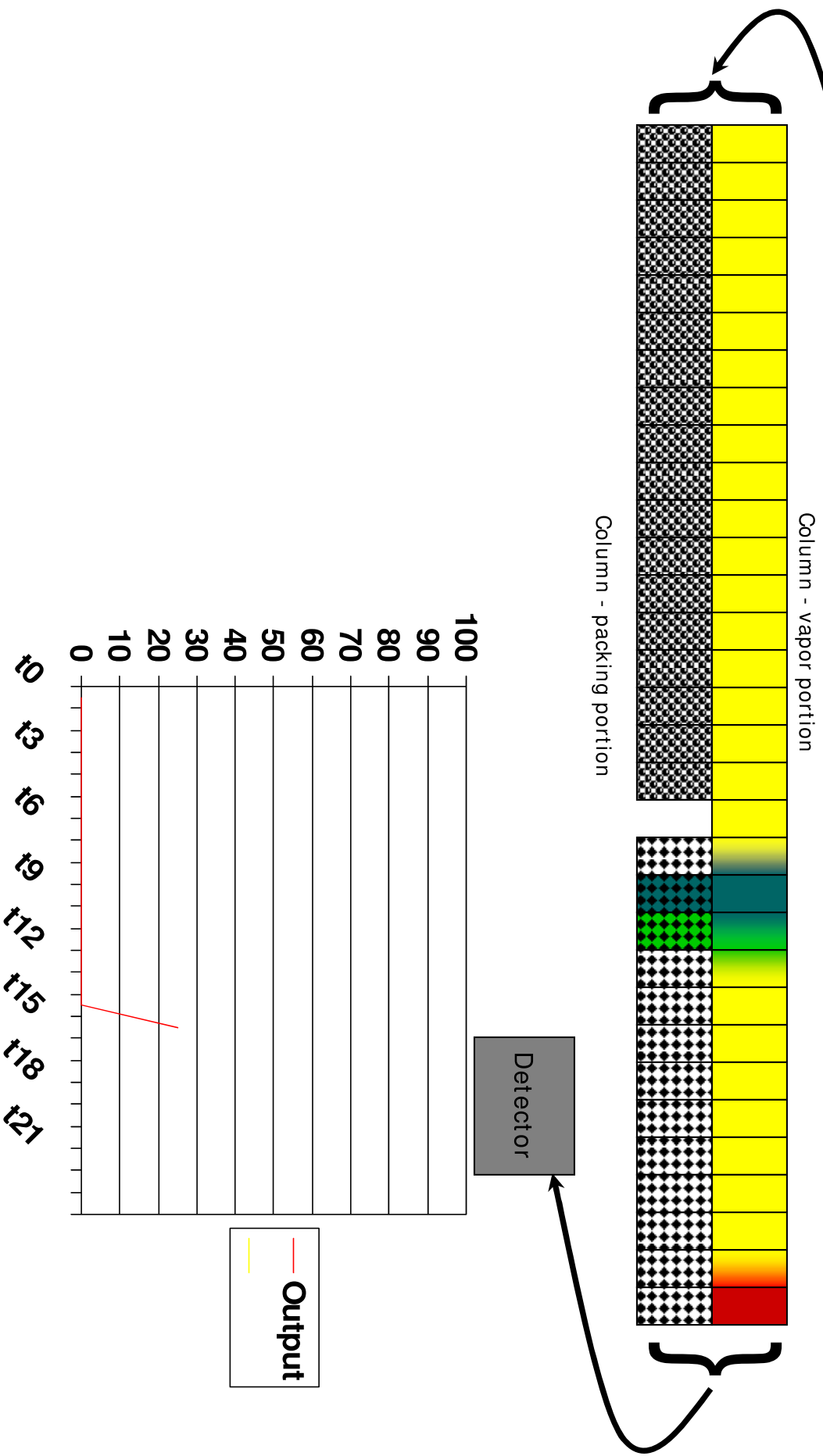
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What Happened

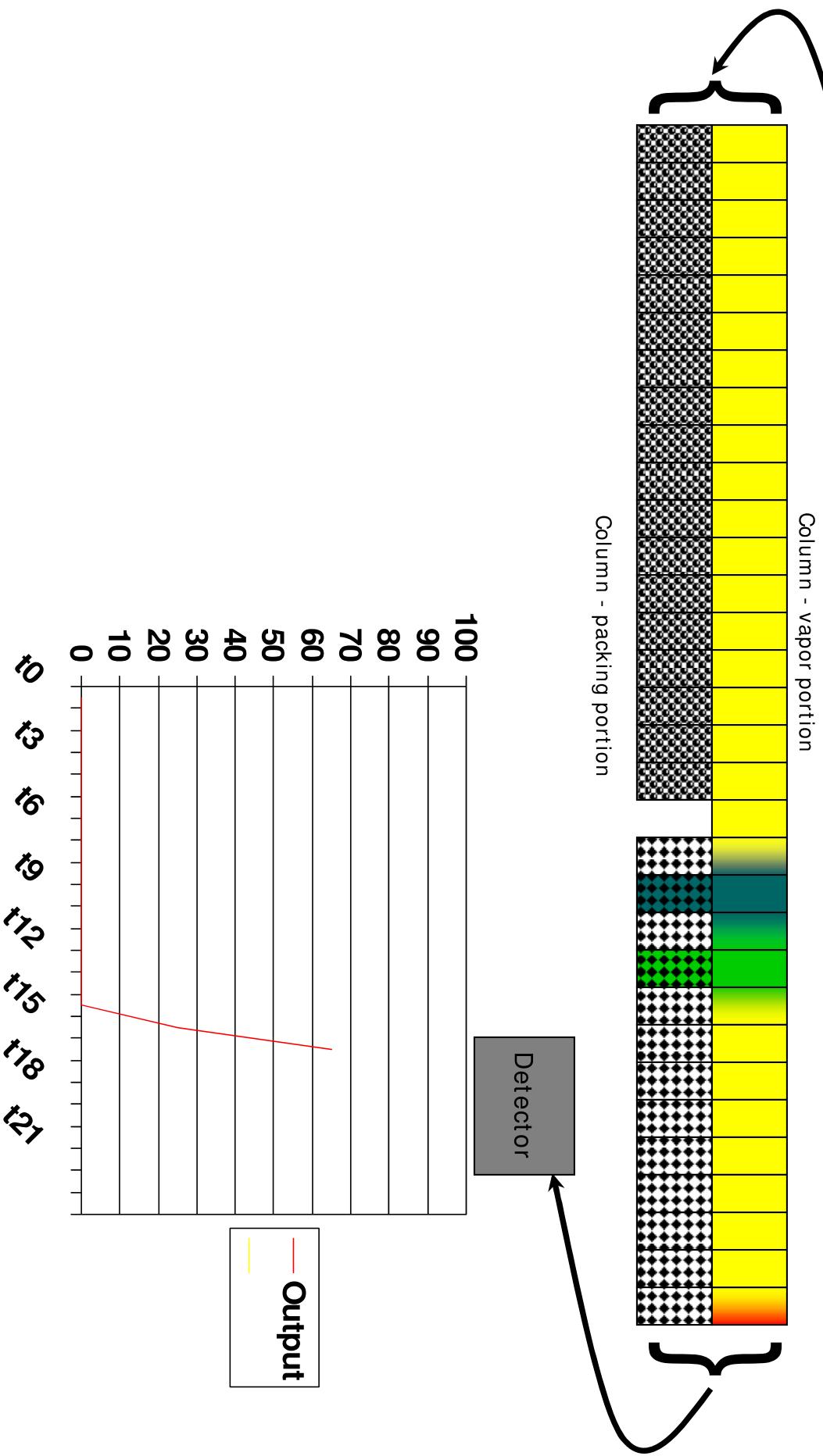
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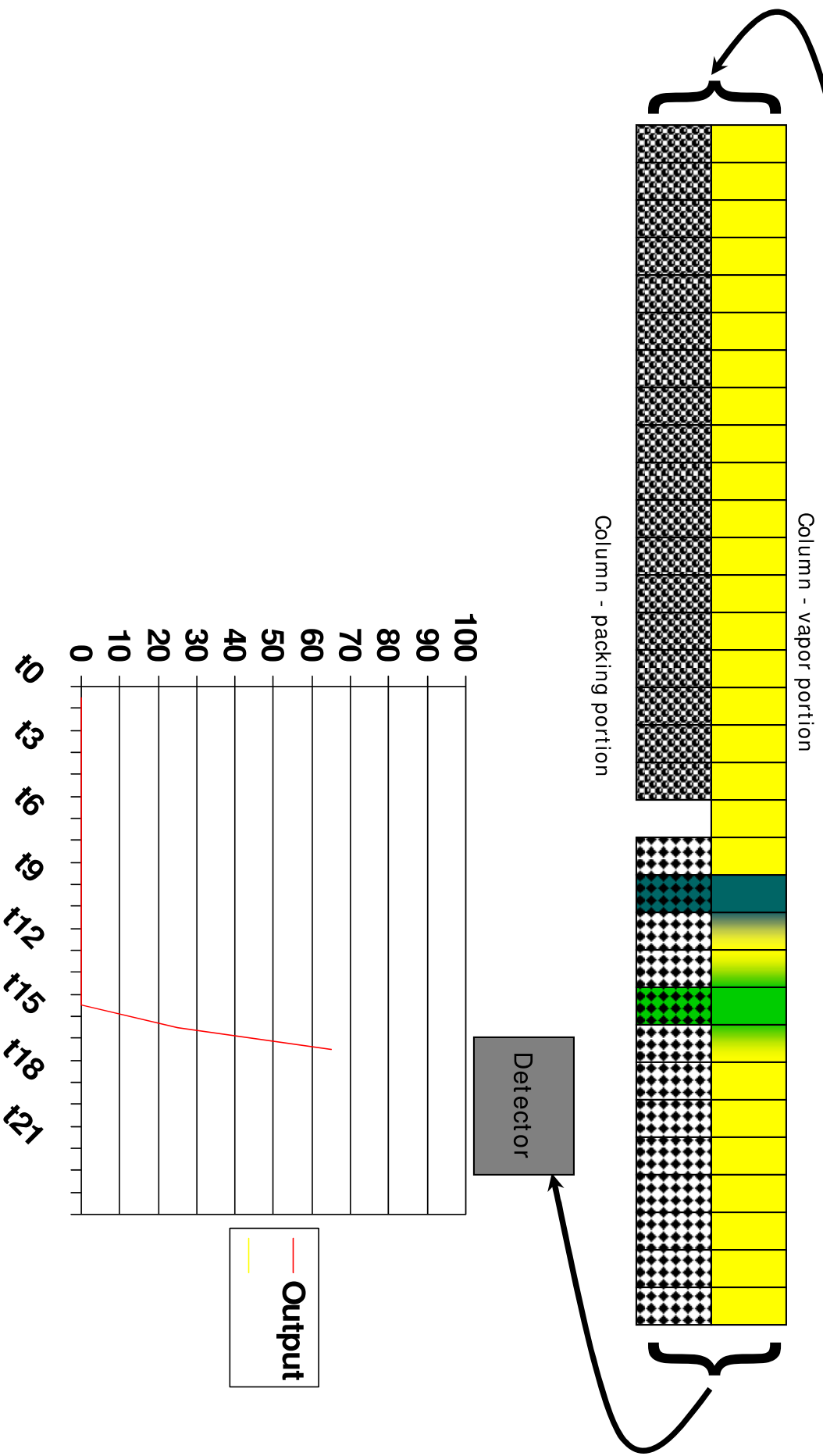
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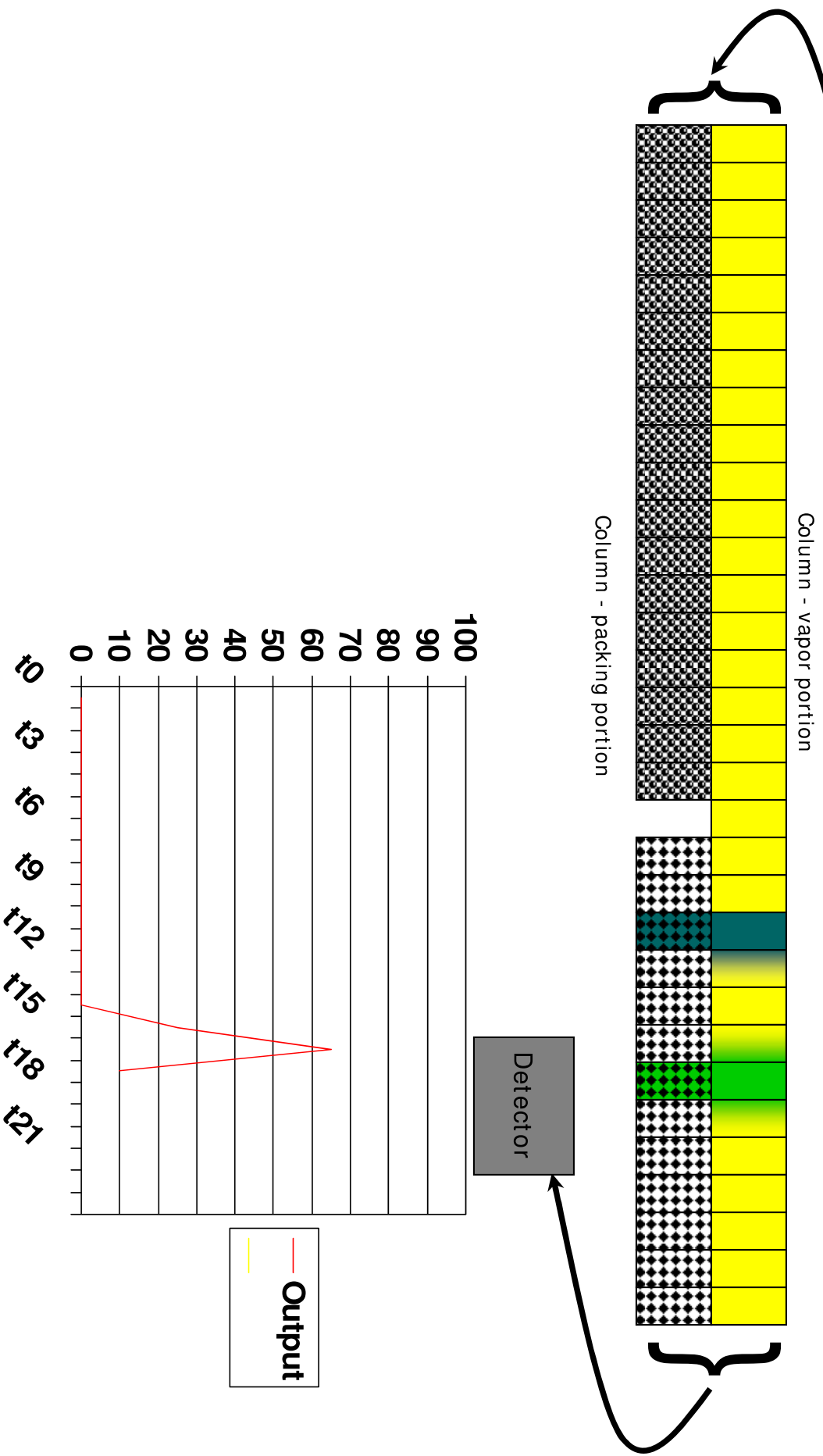
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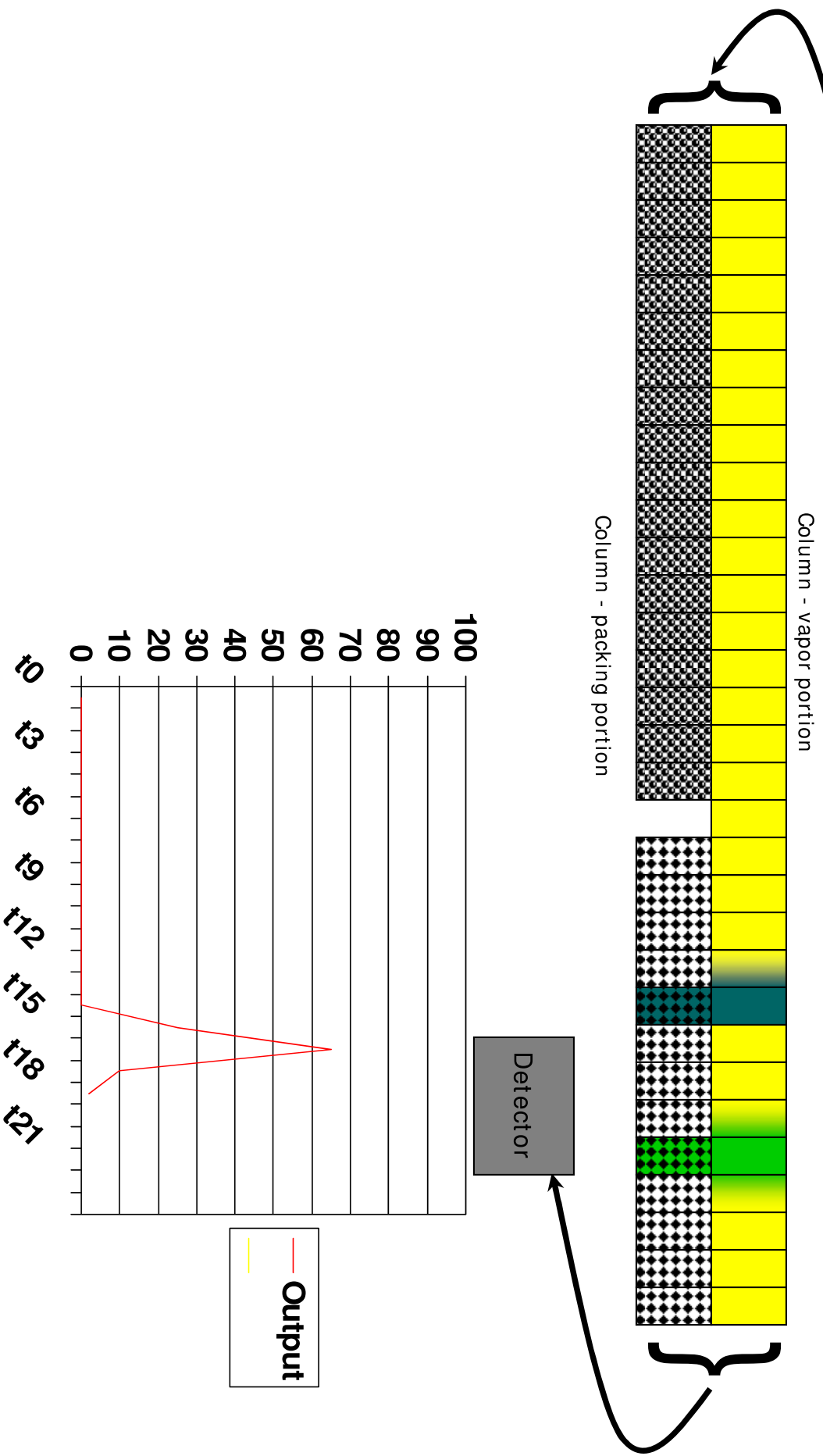
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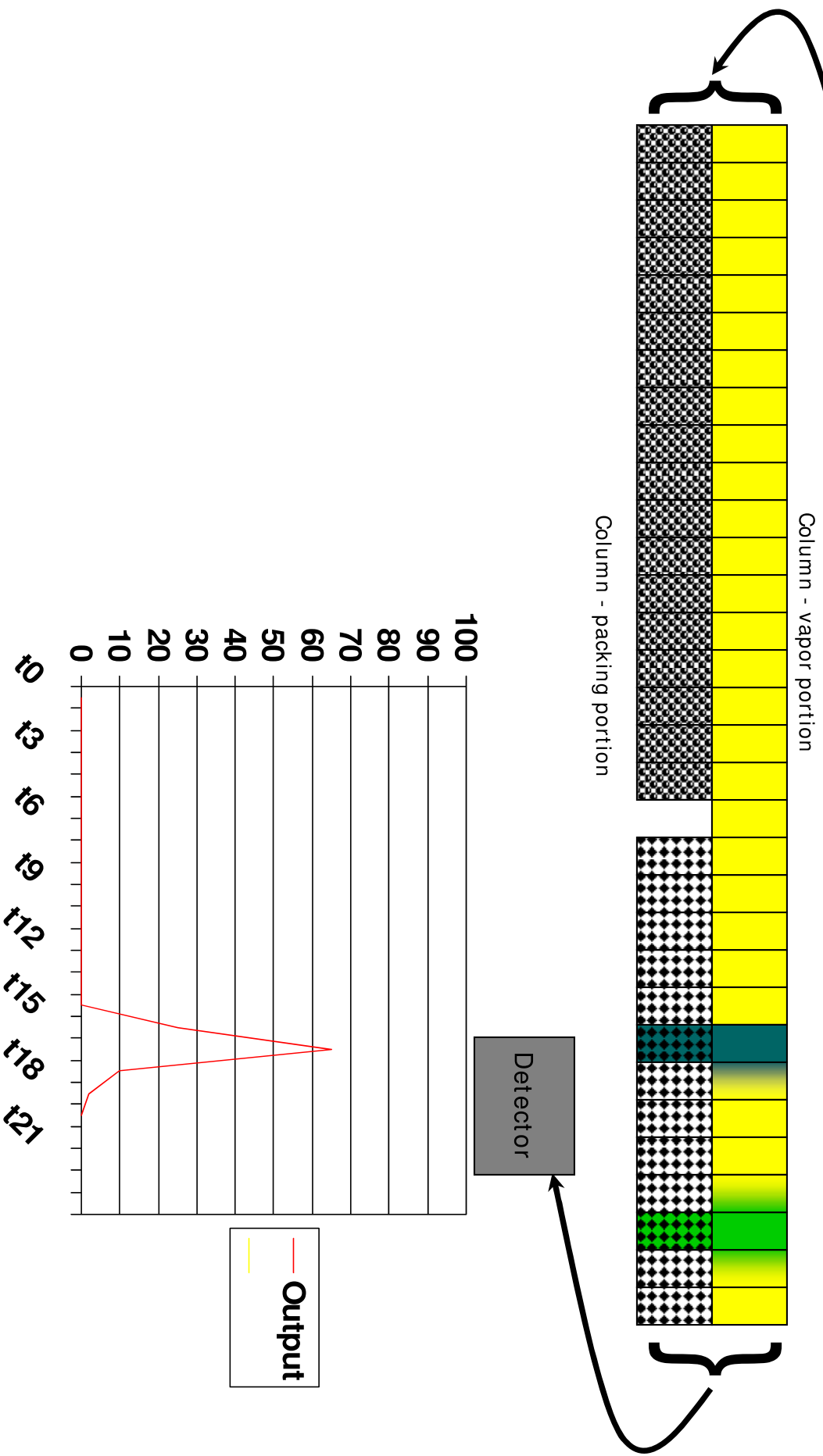
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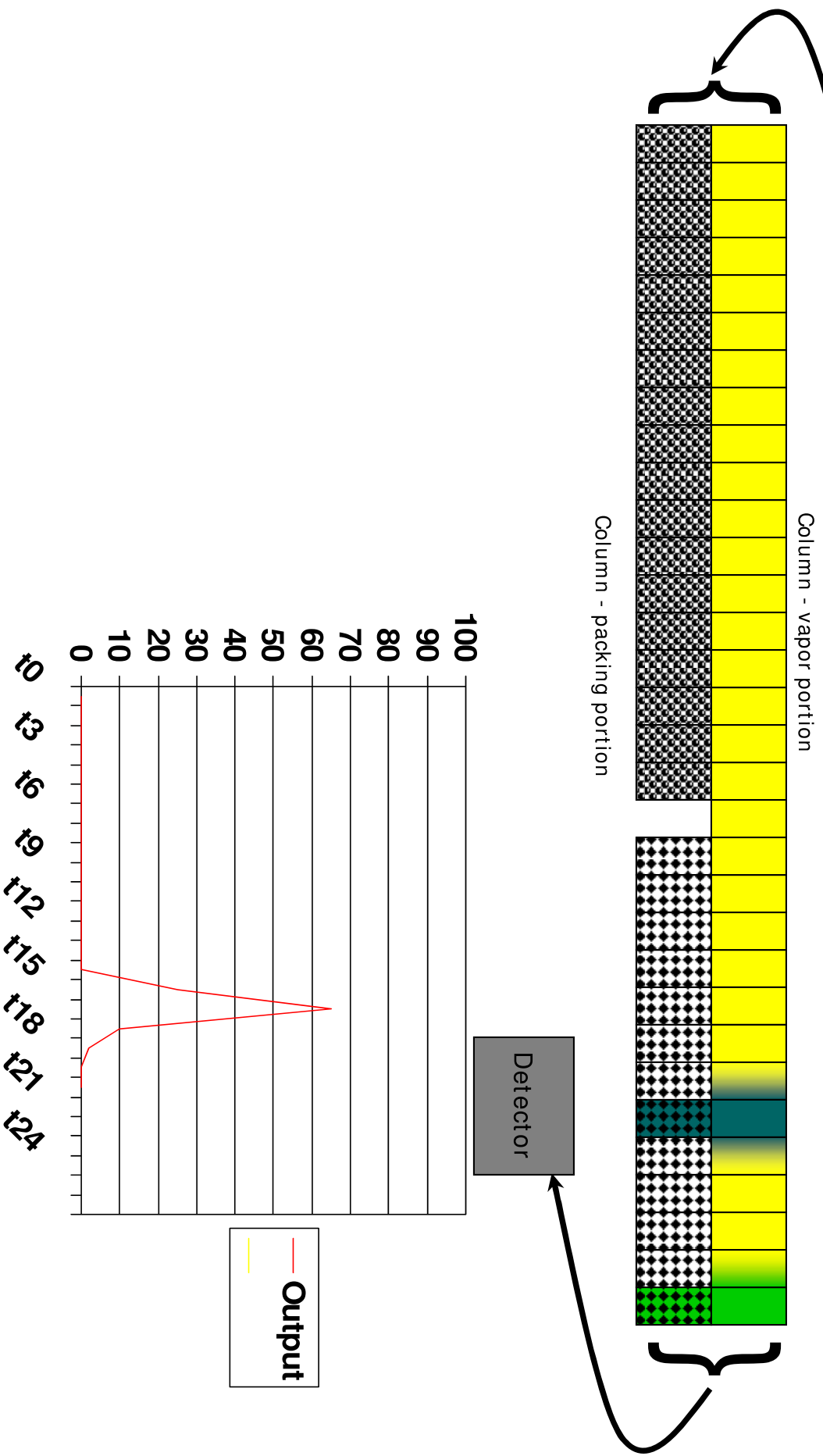
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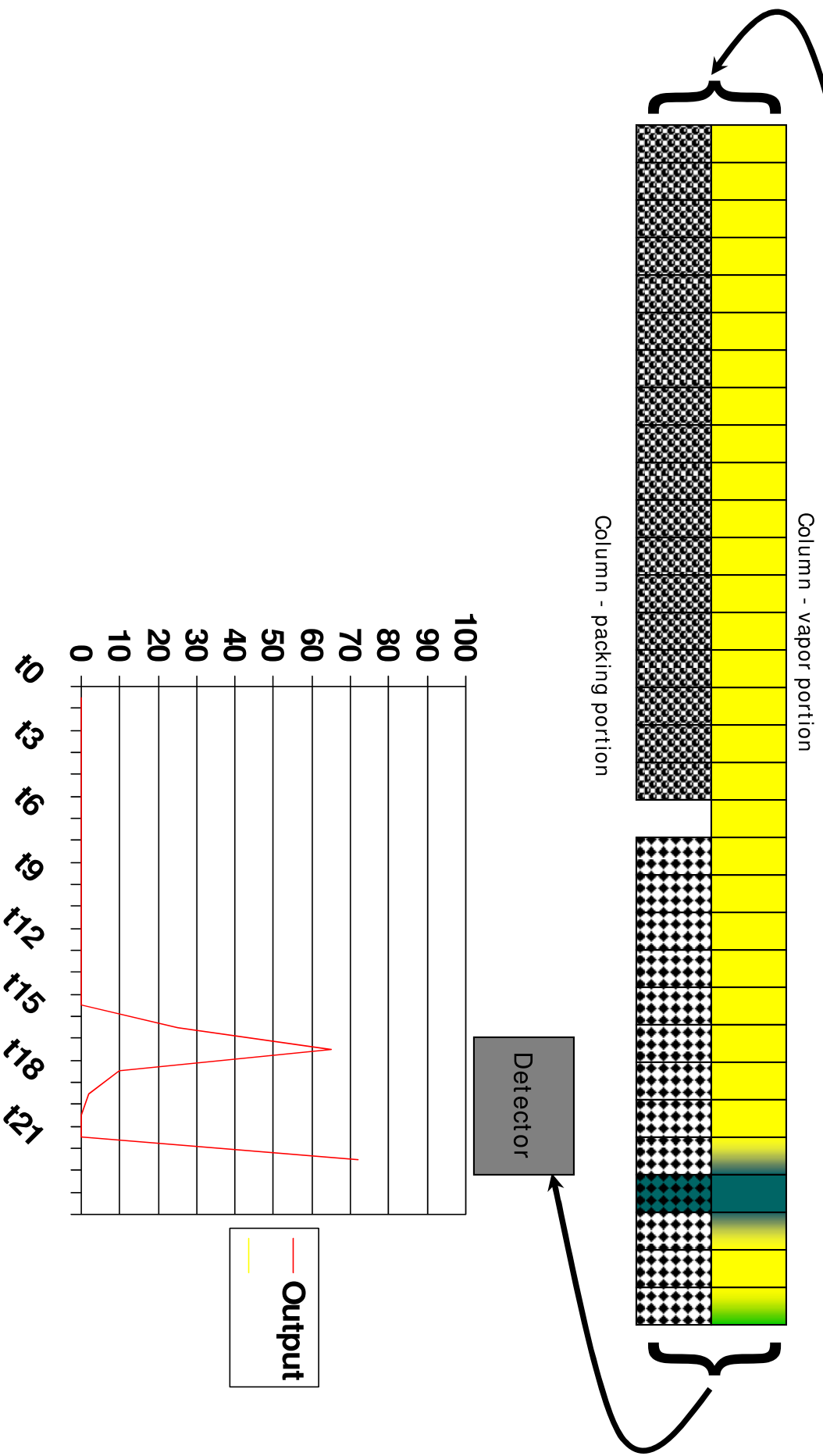
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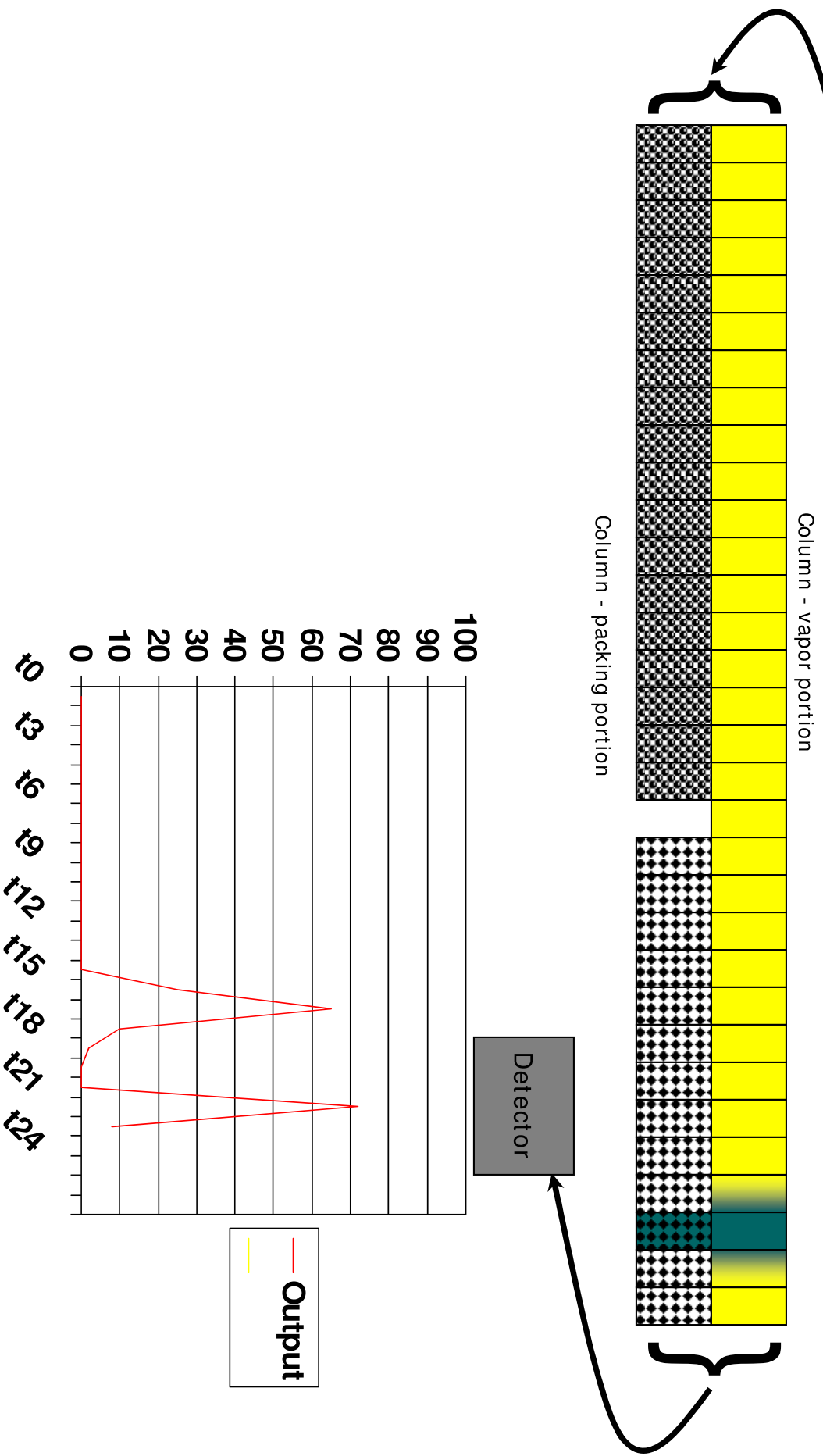
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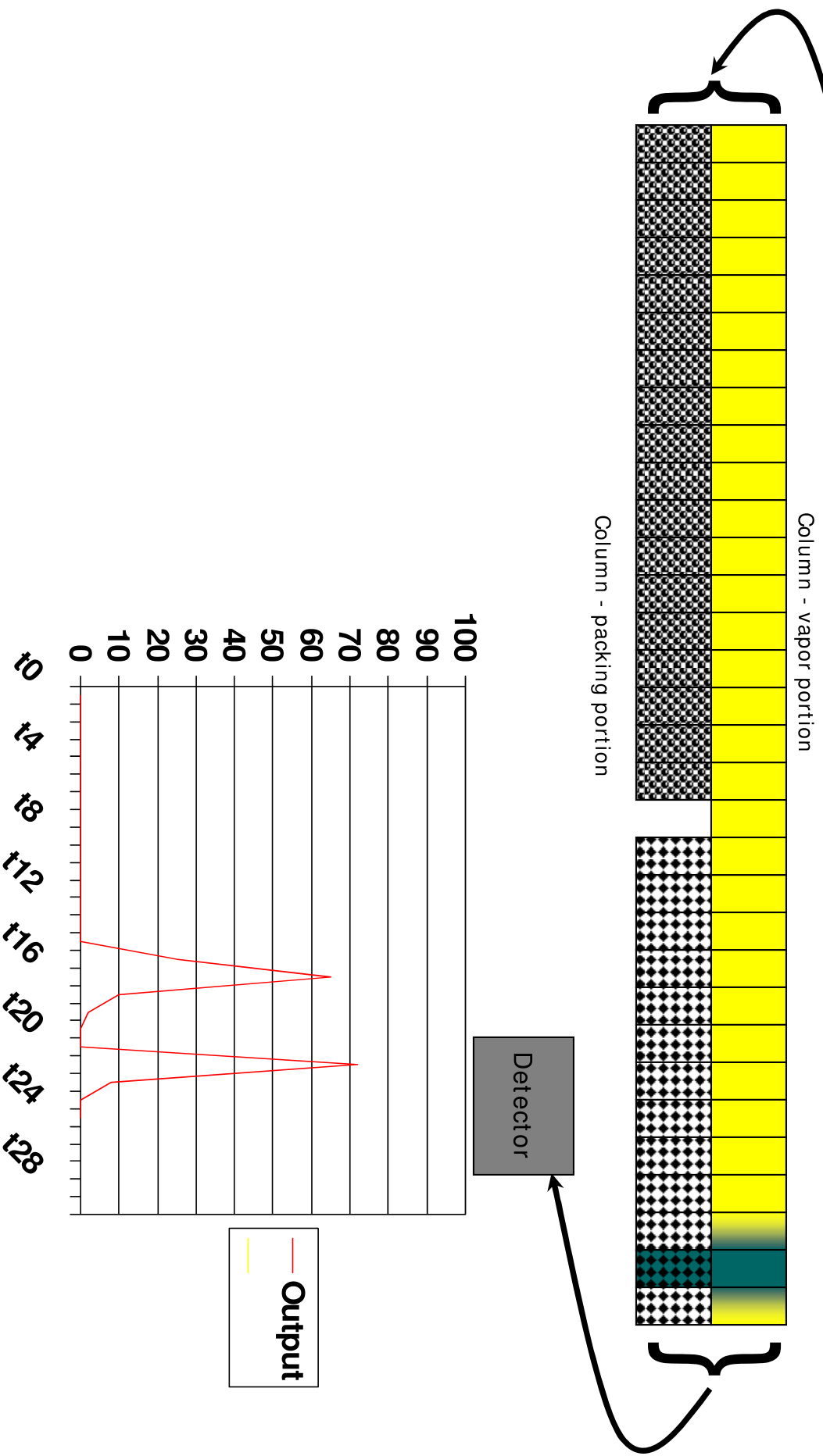
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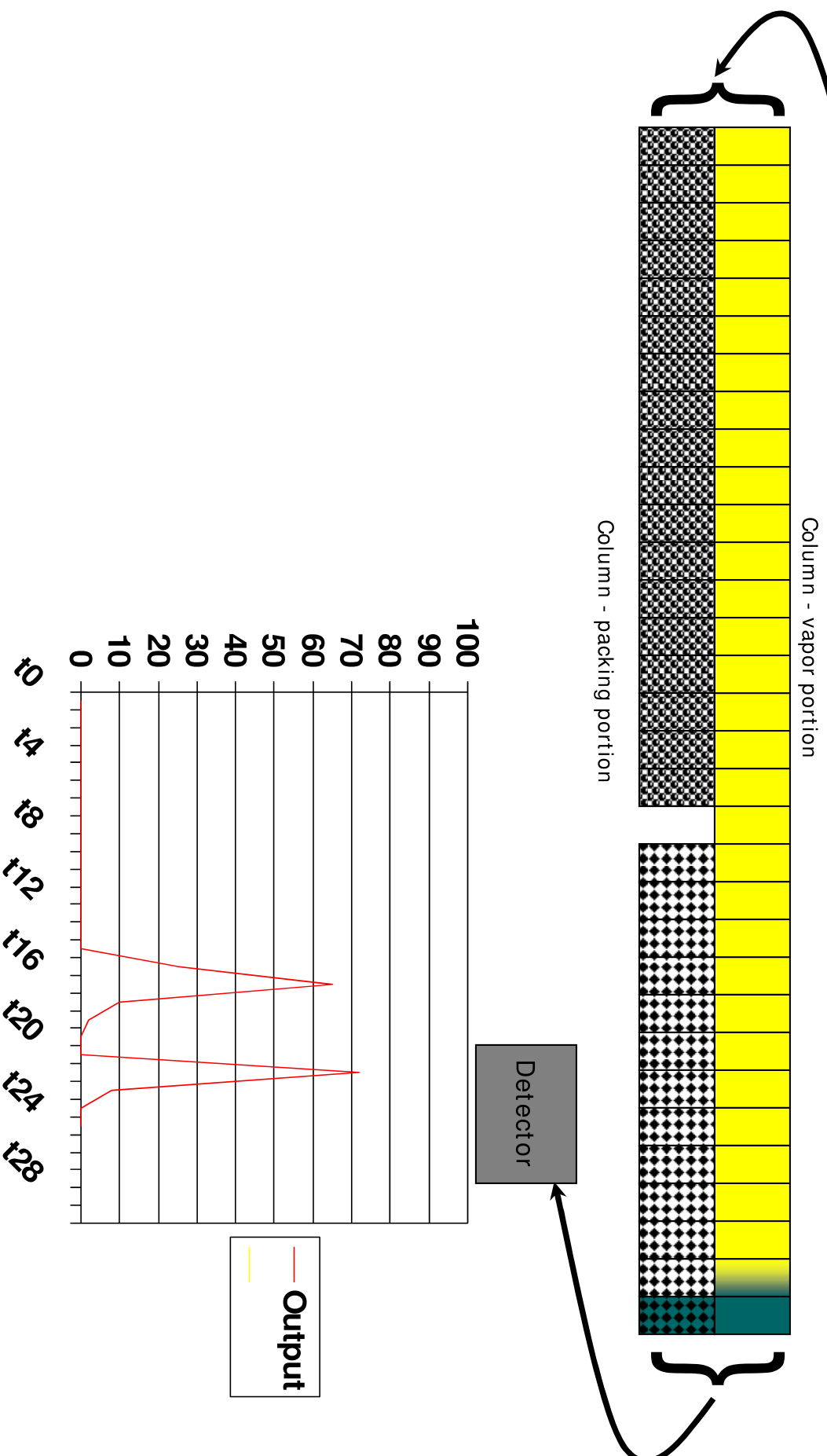
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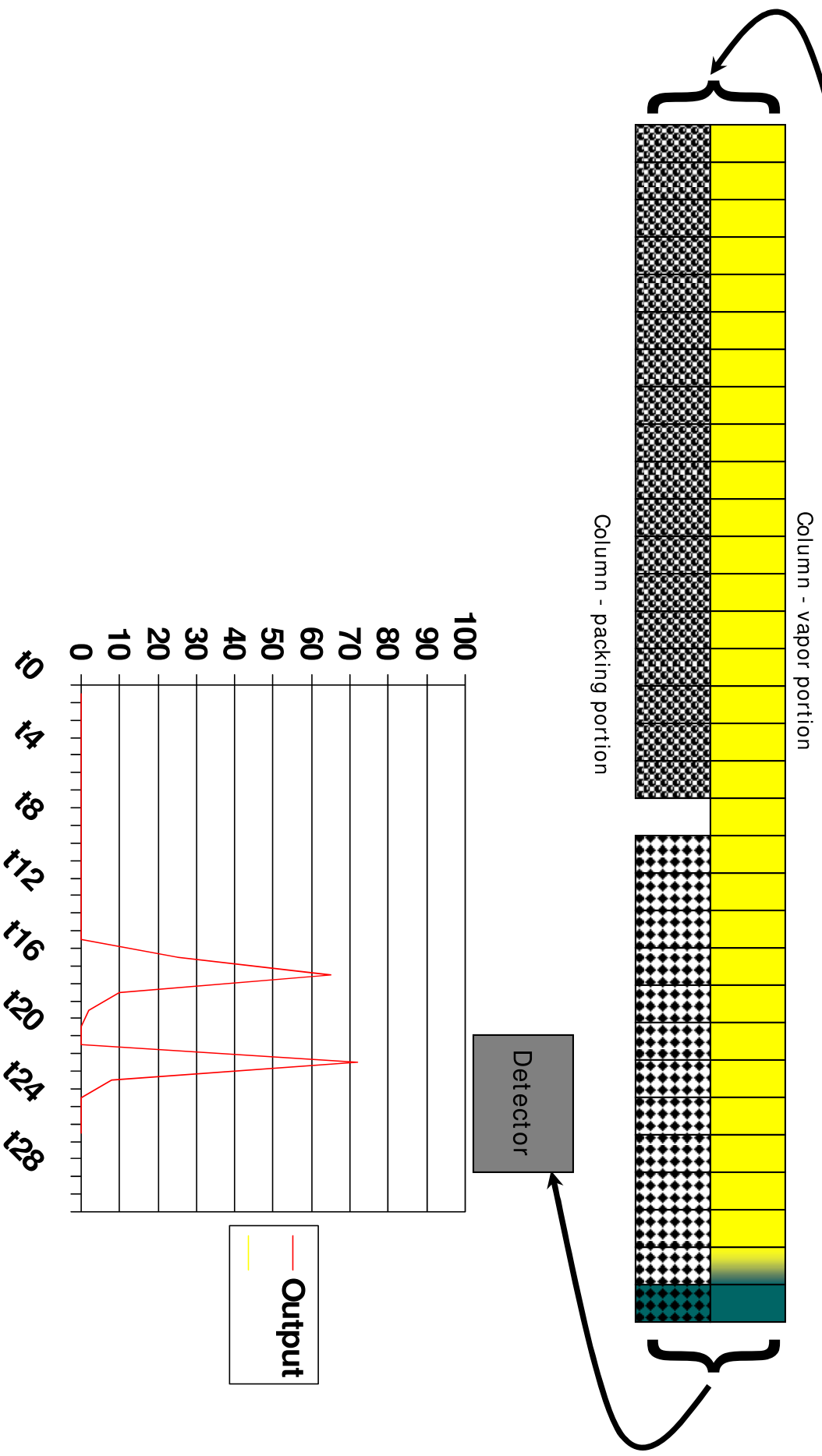
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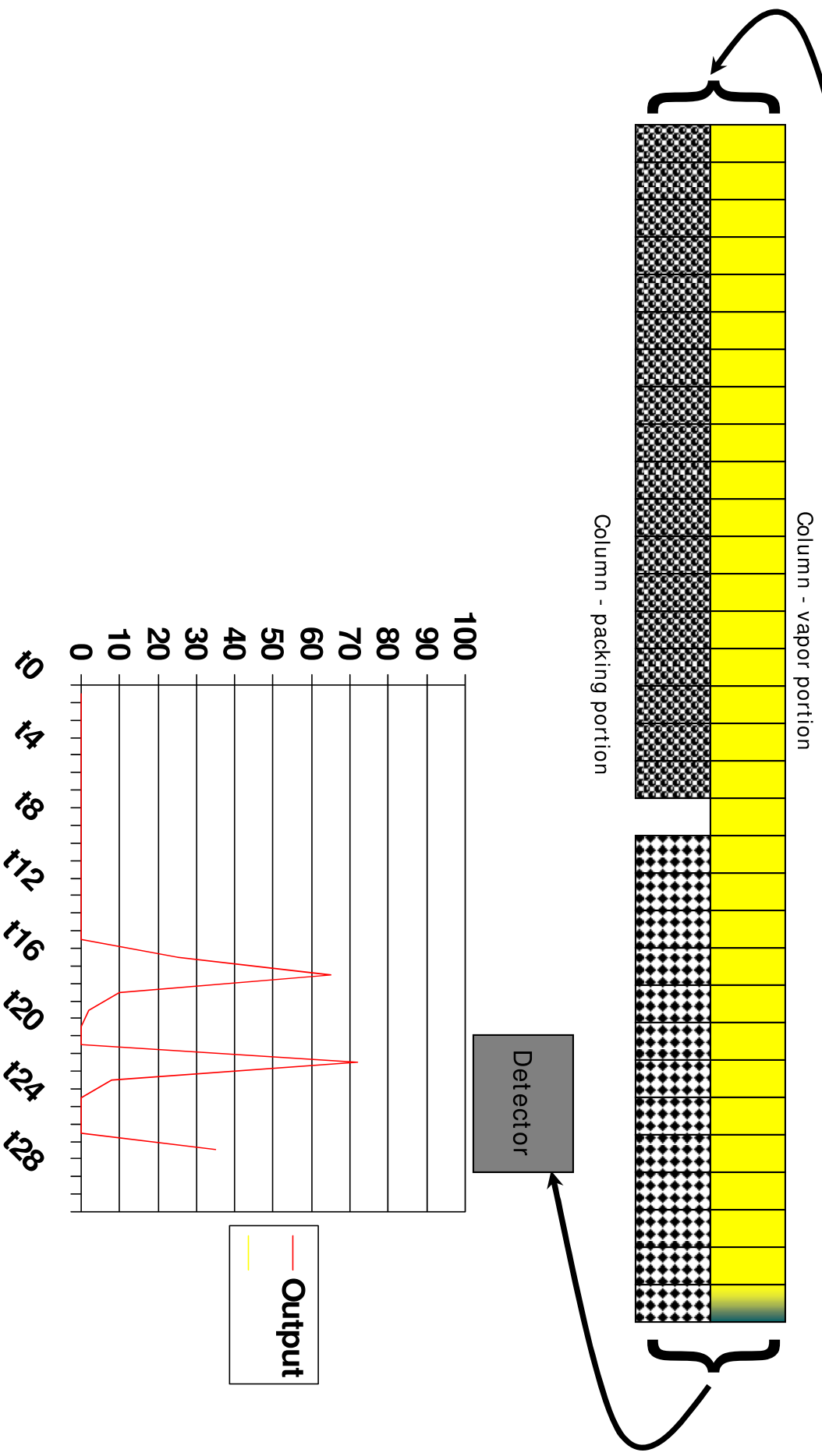
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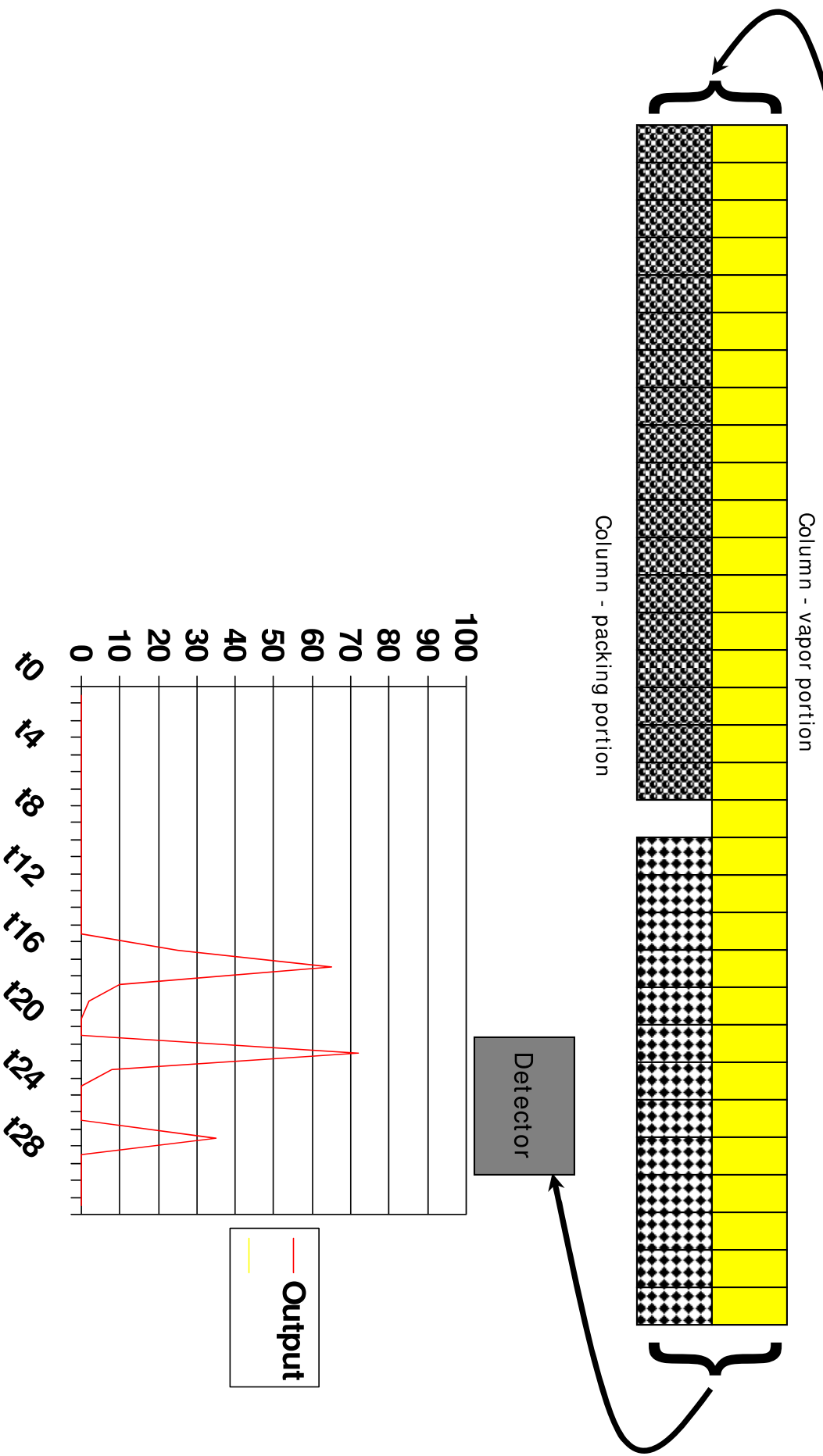
Carrier and sample enter





What Happened

Carrier and sample enter





What are my choices in parts?

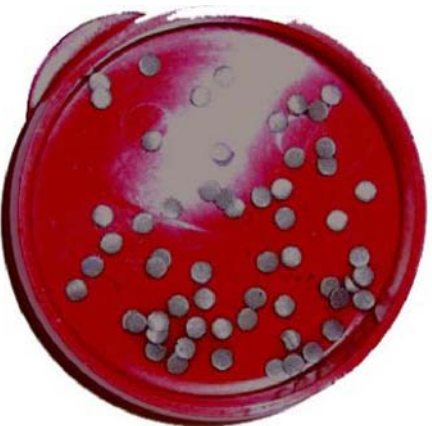
What are my concerns with these parts?

Columns

❖ Packed

- “Standard” 1/8th inch
 - “Micro-pack” 1/16th inch
- ### ❖ Capillary

❖



Column material

Hydrocarbons and sulfur gases

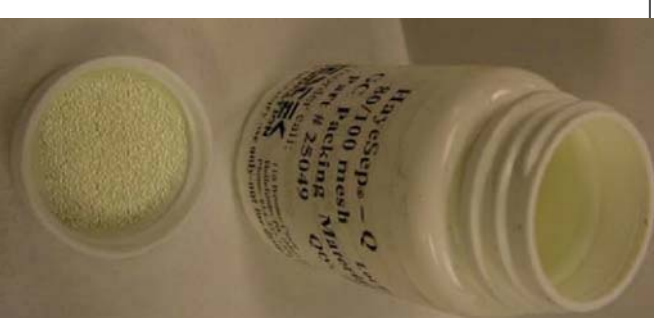
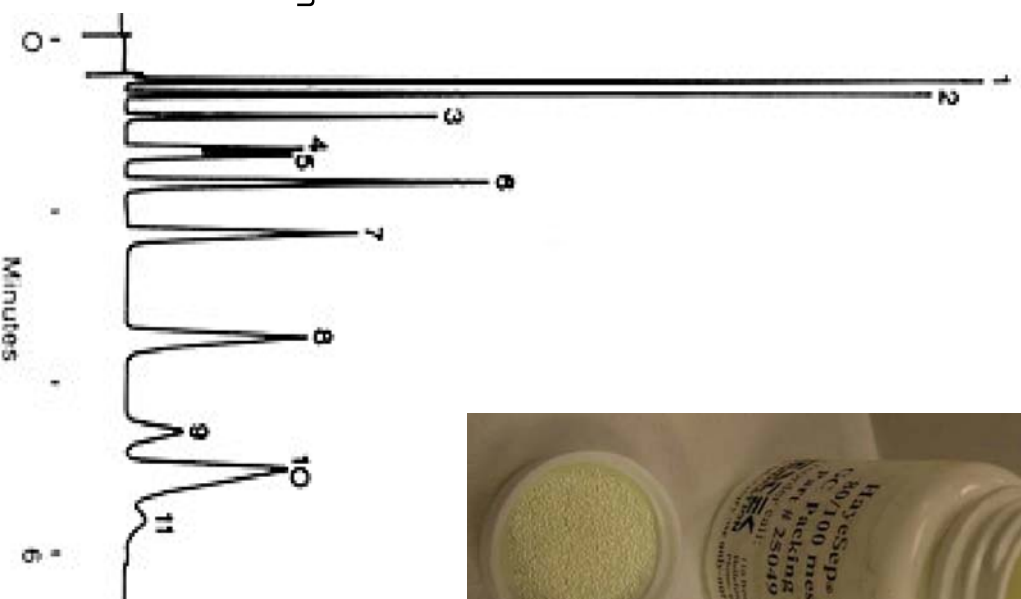
HayeSep[®] Q, 80/100 mesh

1. Air
2. Methane
3. Carbon dioxide
4. Ethylene
5. Acetylene
6. Ethane
7. Hydrogen sulfide
8. Carbonyl sulfide
9. Propylene
10. Propane
11. Propadiene

Column: 8' x 1/8" packed with HayeSep Q, 80/100 mesh

Column temp: 90° C

Flow: He 30 cc/min

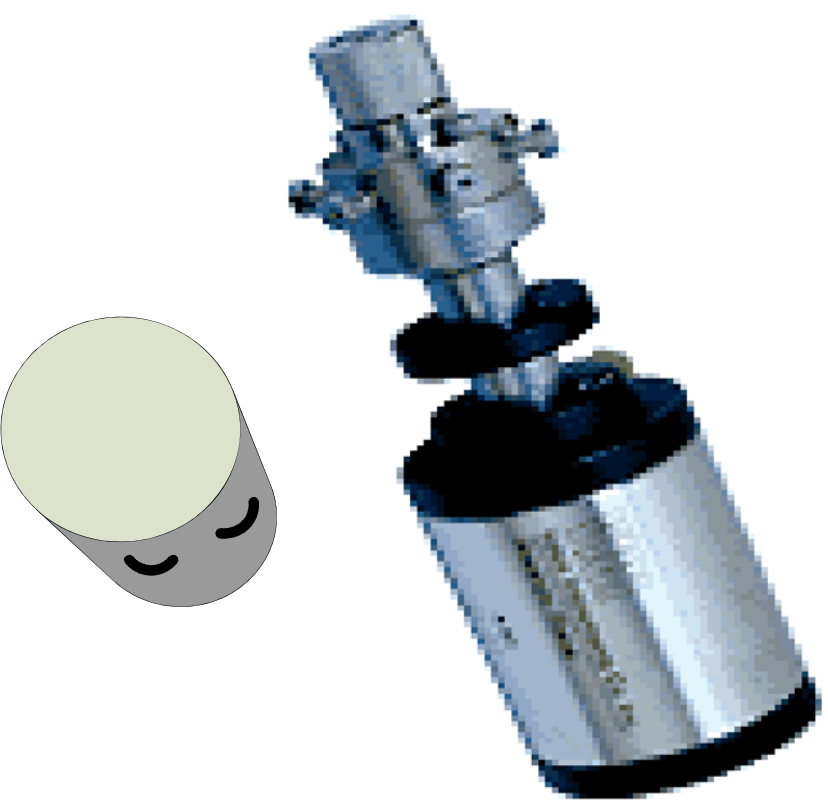


Column material - Liquid

- ✚ Example here would be OV-101
 - Part of the defined column
 - This is Methyl Silicone
 - Gets applied by using Toluene as a solvent
 - Toluene can't be part of the sample.
 - Part of the cross checking application labs have to do.
 - **Stable to about 350°C**
- ✚ Can be coated directly on a column or capillary
- ✚ Can be coated on to a sub-straight and then Packed into the column

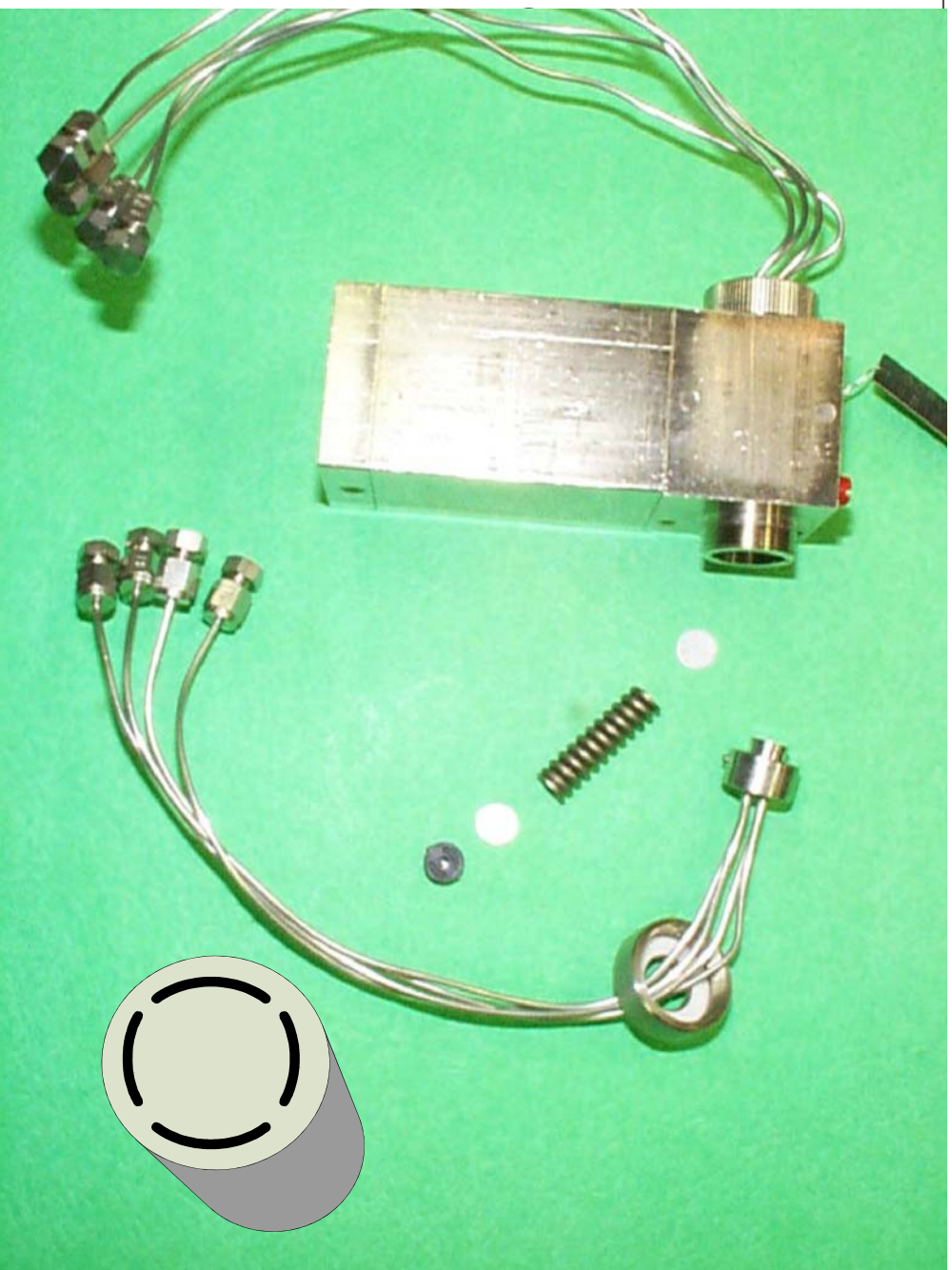
Types of Sample/Oven Valves

- ⇒ Rotary
 - Edge
 - **Face**
- ⇒ Slide
- ⇒ Spool Valves (piston)
- ⇒ Diaphragm



Types of Sample/Oven Valves

- ⇒ Rotary
 - **Edge**
 - Face
- ⇒ Slide
- ⇒ Spool Valve (piston)
- ⇒ Diaphragm



Types of Sample/Oven Valves

Sample
Loop

Rotary

- **Edge**
- **Face**

Slide

Sample In
Carrier In

Seal

Slide

Seal

To
Column

Spool Valves (piston) Diaphragm

Sample In

Seal

Seal

Carrier In

Slide

Types of Sample/Oven Valves

Rotary

- **Edge**
- **Face**

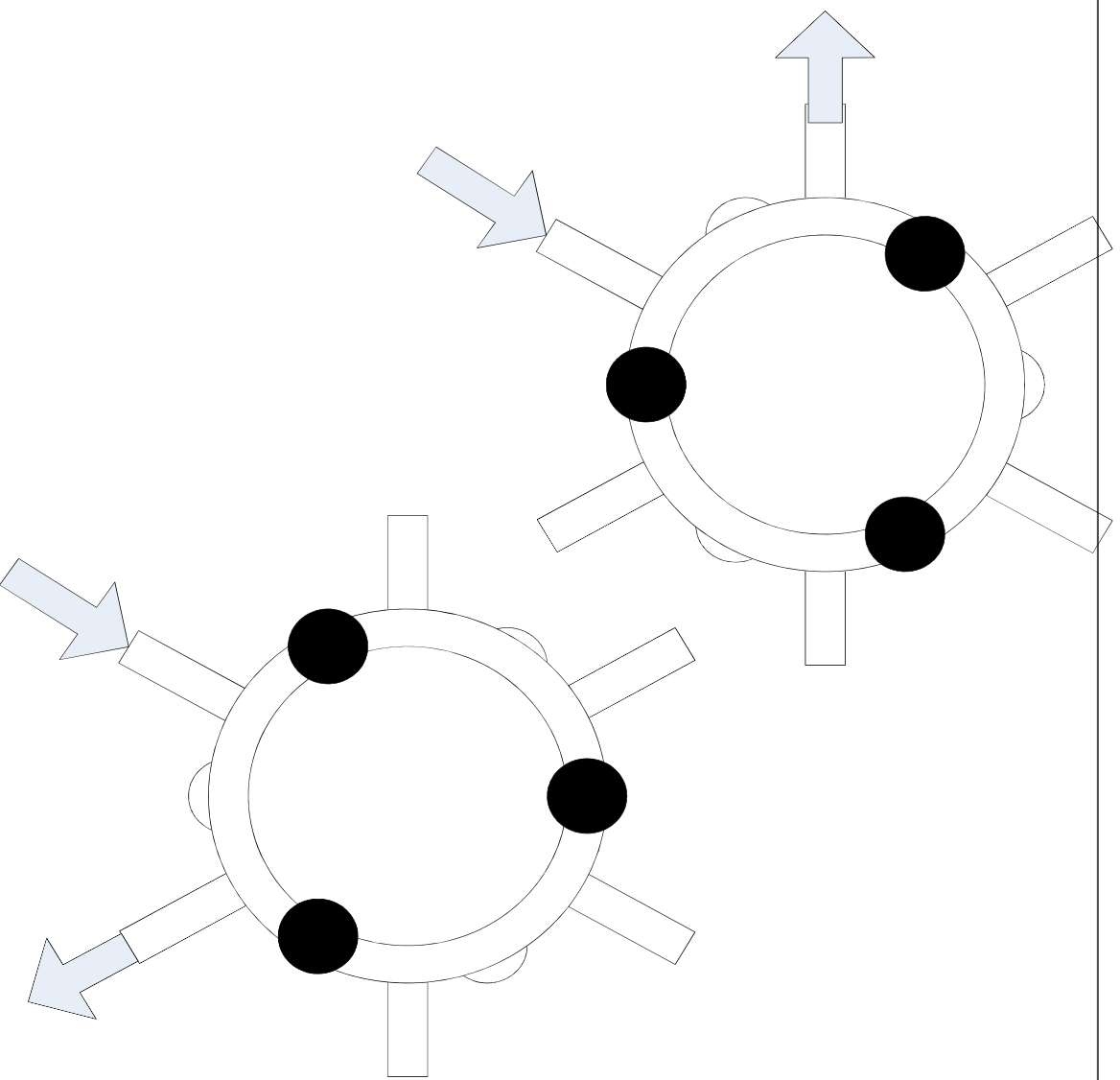
Slide

Spool Valves
(piston)

Diaphragm

Types of Sample/Oven Valves

- ⇒ Rotary
 - **Edge**
 - **Face**
- ⇒ Slide
- ⇒ Spool Valves (piston)
- ⇒ Diaphragm



Ford or Chevy

- ✧ Valves have always been an emotional thing
- ✧ Most work fine – if they are maintained.
- ✧ Some thoughts on valves:
 - #1 – need some kind of **Fail-safe operation**
 - **Rotary**
 - Edge
 - Face
 - **Slide**
 - **Spool Valves (piston)**
 - **Diaphragm**

Detectors

- ❖ In theory all detectors are same = differential
 - **Measure difference between carrier and sample**
- ❖ TCD
- ❖ FID
- ❖ FPD
- ❖ PID
- ❖ Others
 - **Hard to maintain 24/7 so rare**



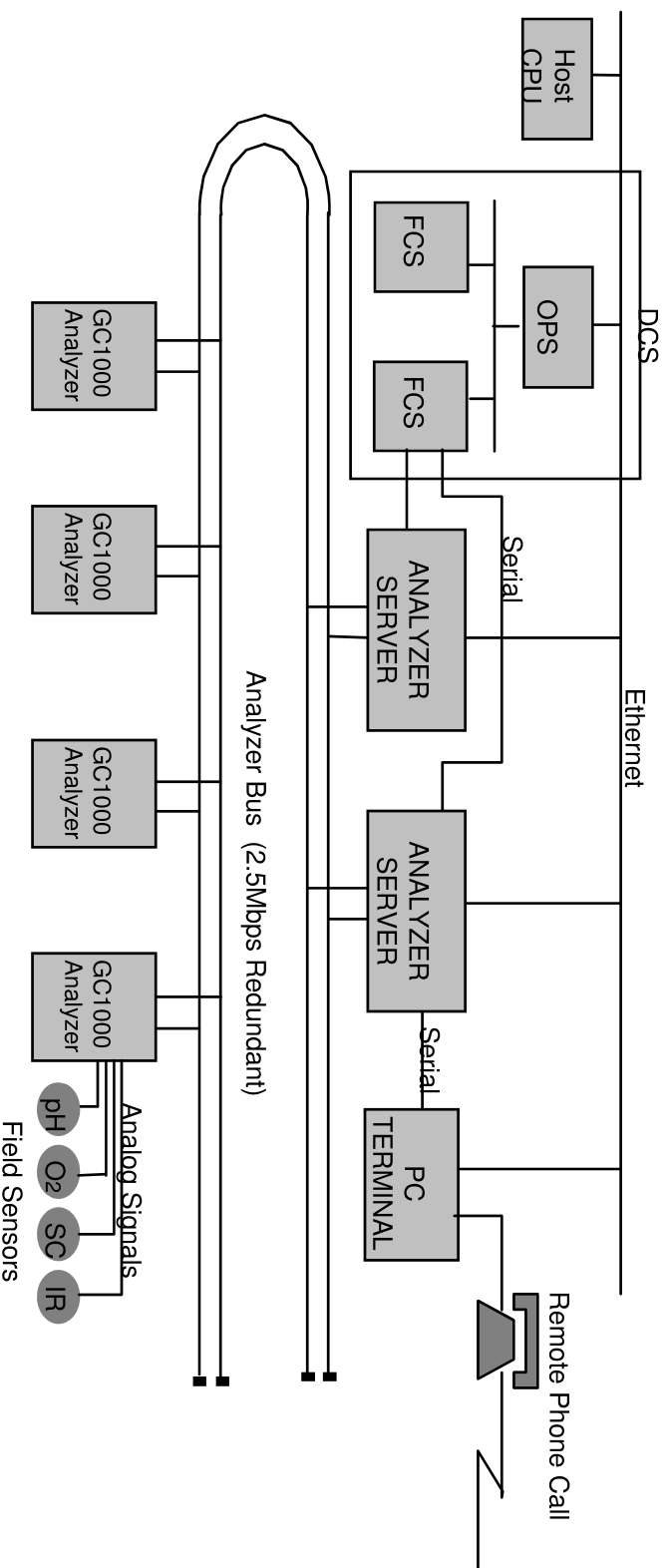
Communications

- ❖ **Modbus**
 - **OPC**
 - **Ethernet**
- ❖ **Ethernet**



Classical Communications

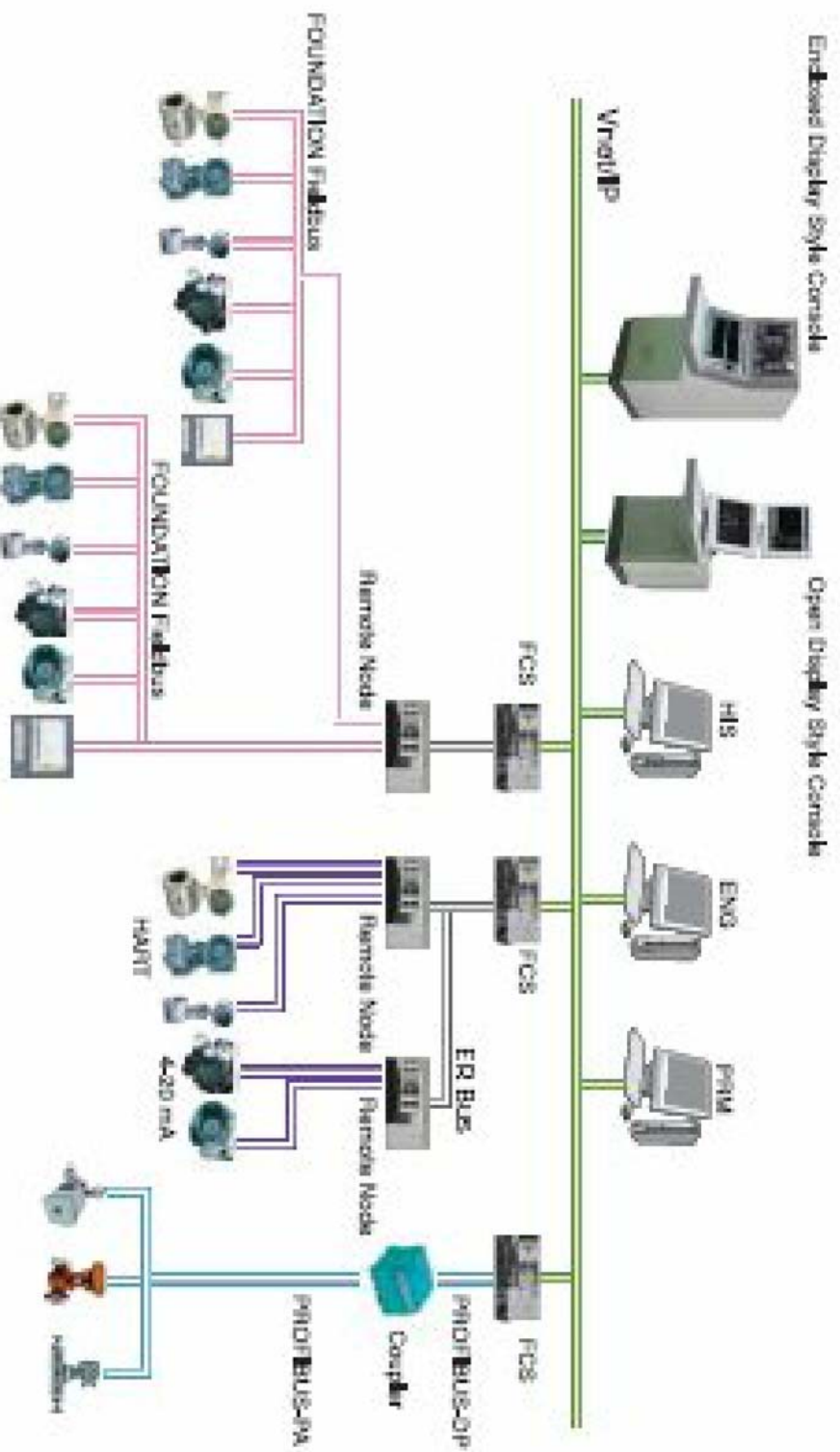
- ❖ 4-20ma outputs
- ❖ MODBUS RTU
- ❖ Proprietary Networks



Modern Networking

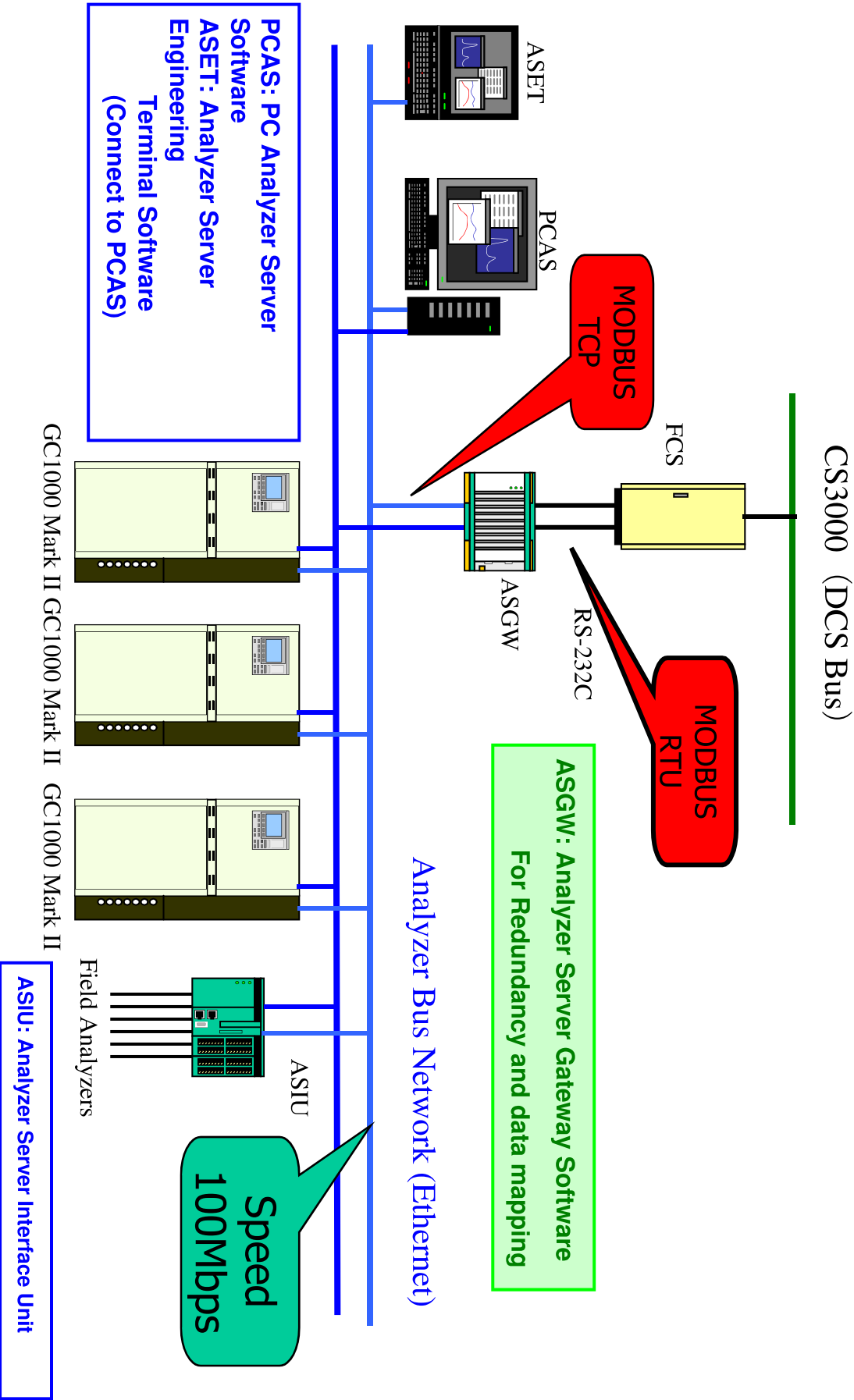
First issue is Fieldbus or not

CENTUM CS 3000 R3



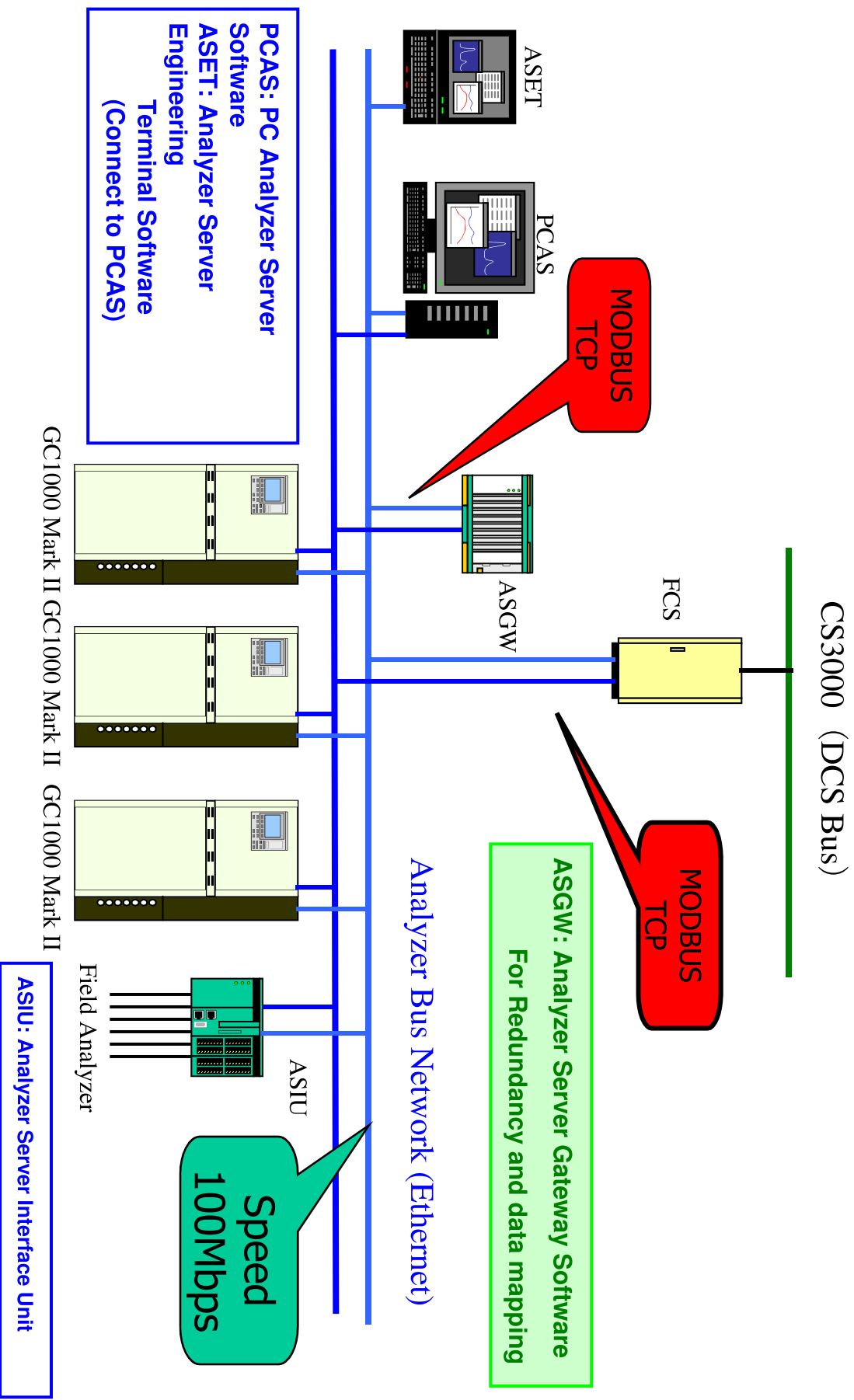


Example of System Config.(2) Duplex comm. 1



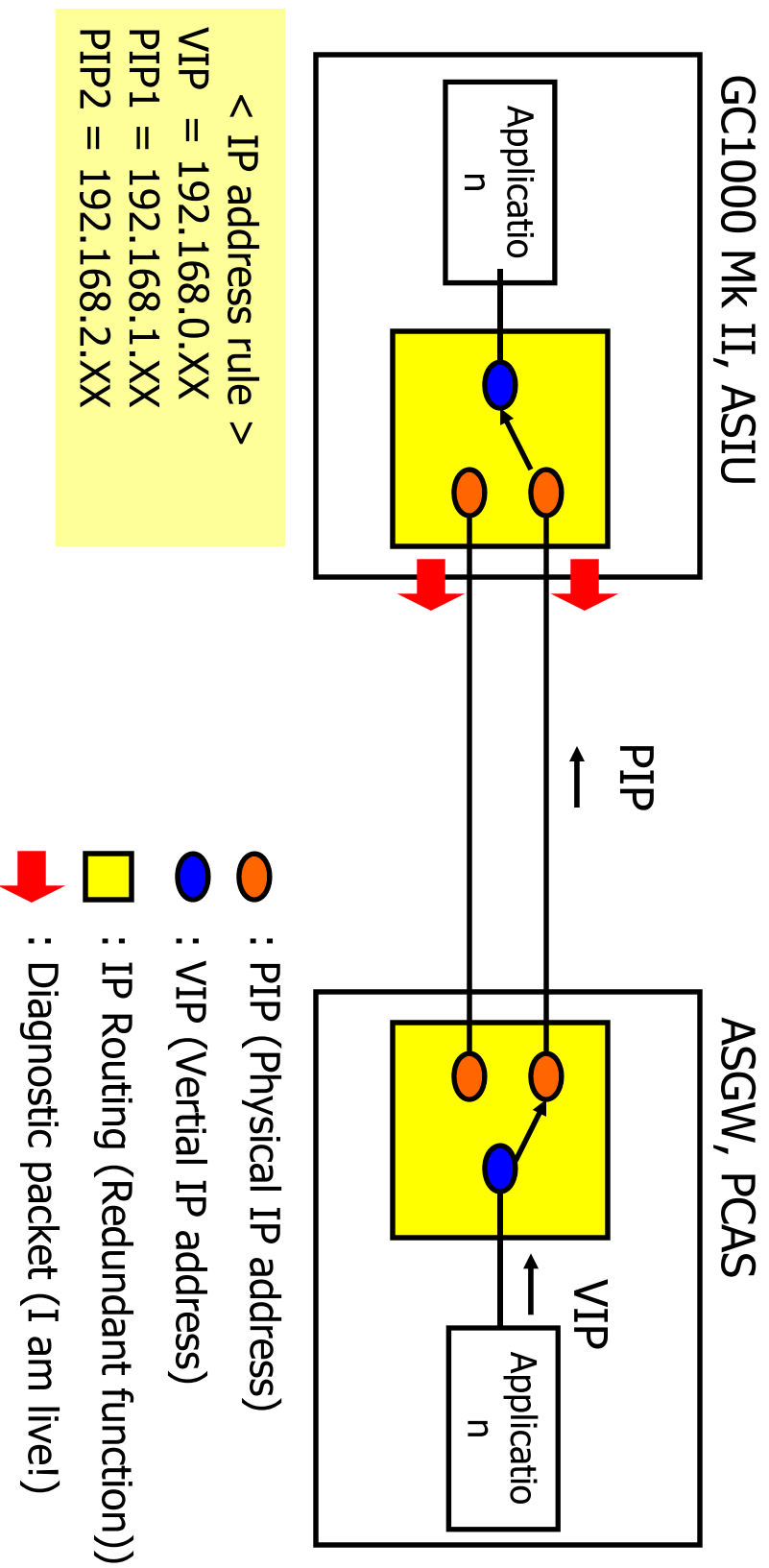


Example of System Config.(3) Duplex comm. 2

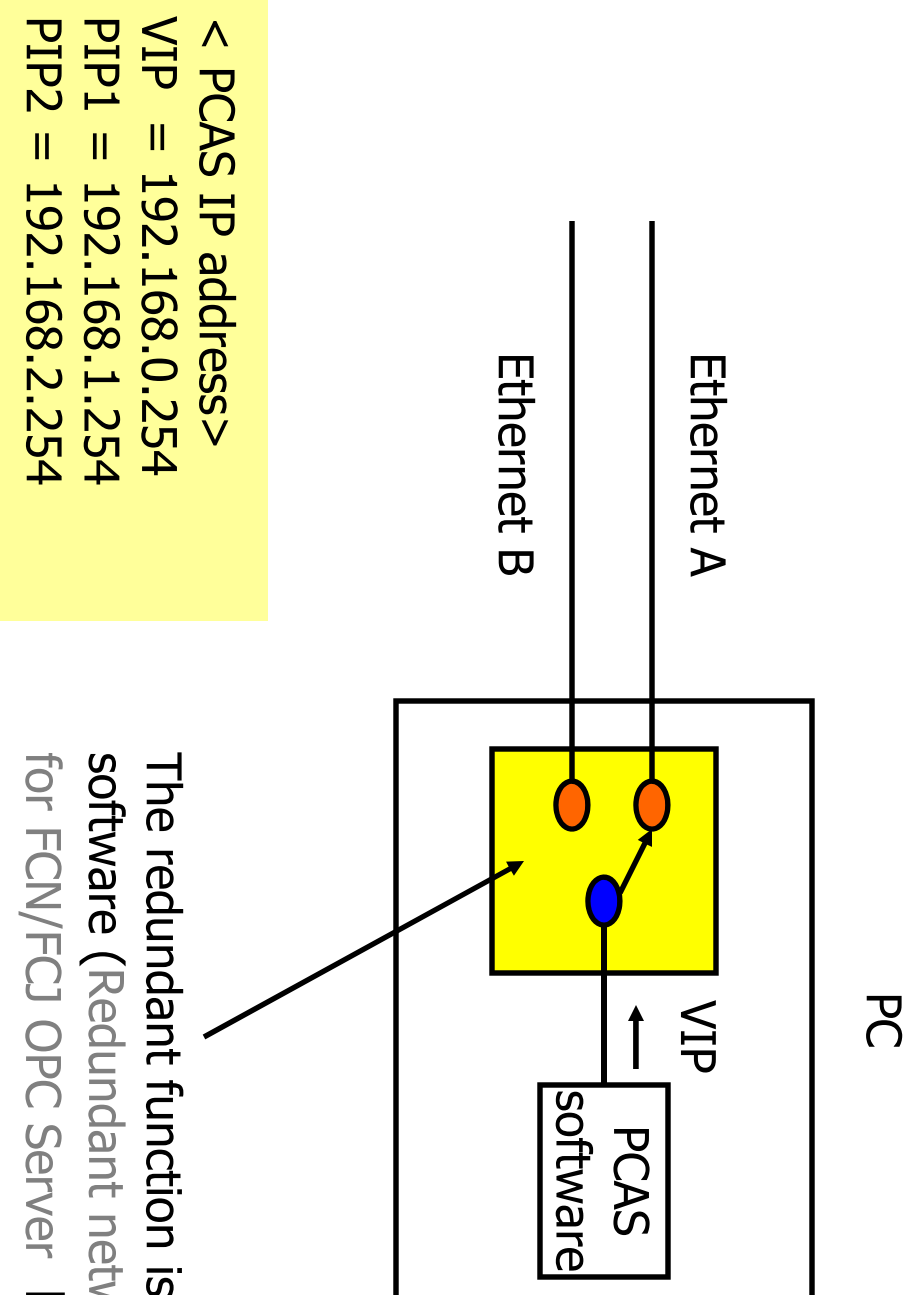


Redundancy between FCJ/PCAS and GC/ASIU

1. ASGW/PCAS tries to connect to GC/ASIU by VIP.
2. PIP is selected automatically by IP routing which has the redundant function.
3. A diagnostic packet is always sent from node to node, so GC/ASIU recognizes which line is live.
4. The connected PIP is connected to the application through VIP.

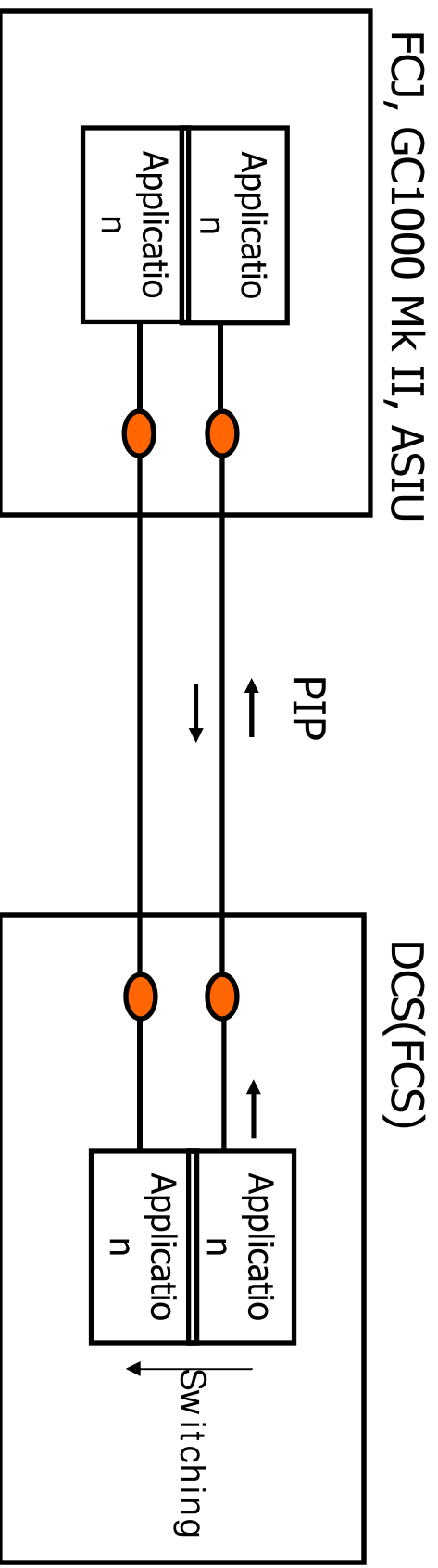


Redundancy for PCAS



Redundancy between DCS and FCJ/GC/ASIU

1. DCS(FCS) connects to FCJ/GC/GCIU by the specified IP address.
2. FCJ/GC/ASIU responds to FCS when connected.
3. When no response from FCJ/GC/ASIU, FCS tries to connect them by the other IP address.
4. FCJ/GC/ASIU responds to FCS when connected.



< IP address >

PIP1 = 192.168.1.XX

PIP2 = 192.168.2.XX

● : PIP (Physical IP address)

Specifications

Network	Ethernet IEEE802.3u 100Base-TX 100Base-FX		
Protocol	TCP/IP		
Communication Rate	100 Mbps		
Media	Shielded TP(STP) or Fiber Optical(FO)		
Connection Type	STP: RJ45 FO: SC		
Duplex	Available with FCJ		
OPC	Available with FCJ		
Number of Node	Maximum 254 on 1 network		
Server	PC with Windows XP or 2000		
Connect to FCS	Direct Ethernet Modbus TCP		
	Modbus RTU with Converter		
	Modbus RTU with FCJ for mapping		
	Modbus TCP with FCJ for mapping		
Input interface	DI/DO 16point AI 16point		

Subject to change without notice



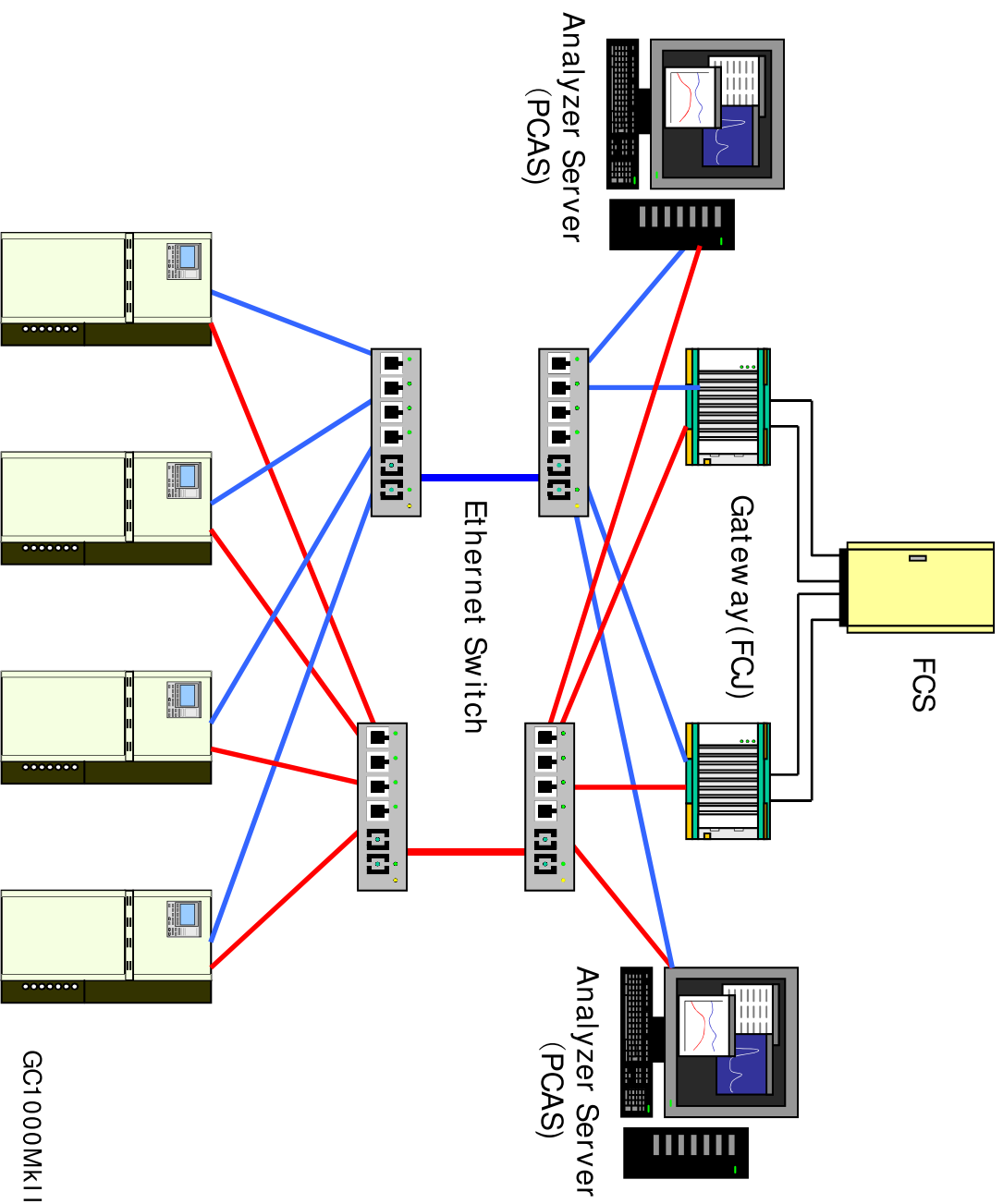
Specifications (Software)

PCAS Analyzer Server Software	Function	Storage of all analytical results for 1 year, all chromatogram for 2 months and every 10th for year, alarms , events (*) Storage rate depends on hard disk space
	Location	on Server PC
	Configuration	max. 64 analyzers connect to 1 Analyzer Server
		max. 14 Analyzer Server on 1 Network
ASET Engineering Terminal Software	Function	For Maintenance and Engineering of GC on Network
	Function	Each analyzer operation and view, and all analyzer overview.
	Operation of	Multi analyzer
	Location	on Server PC or PC on Network
GCET Engineering Terminal Software	Configuration	max.4 Eng.T terminal connect to 1 Analyzer Server
	Function	For Maintenance and Engineering of GC
	Location	Each analyzer operation and view
	Operation of	PC on Network or connected to GC via serial. one analyzer

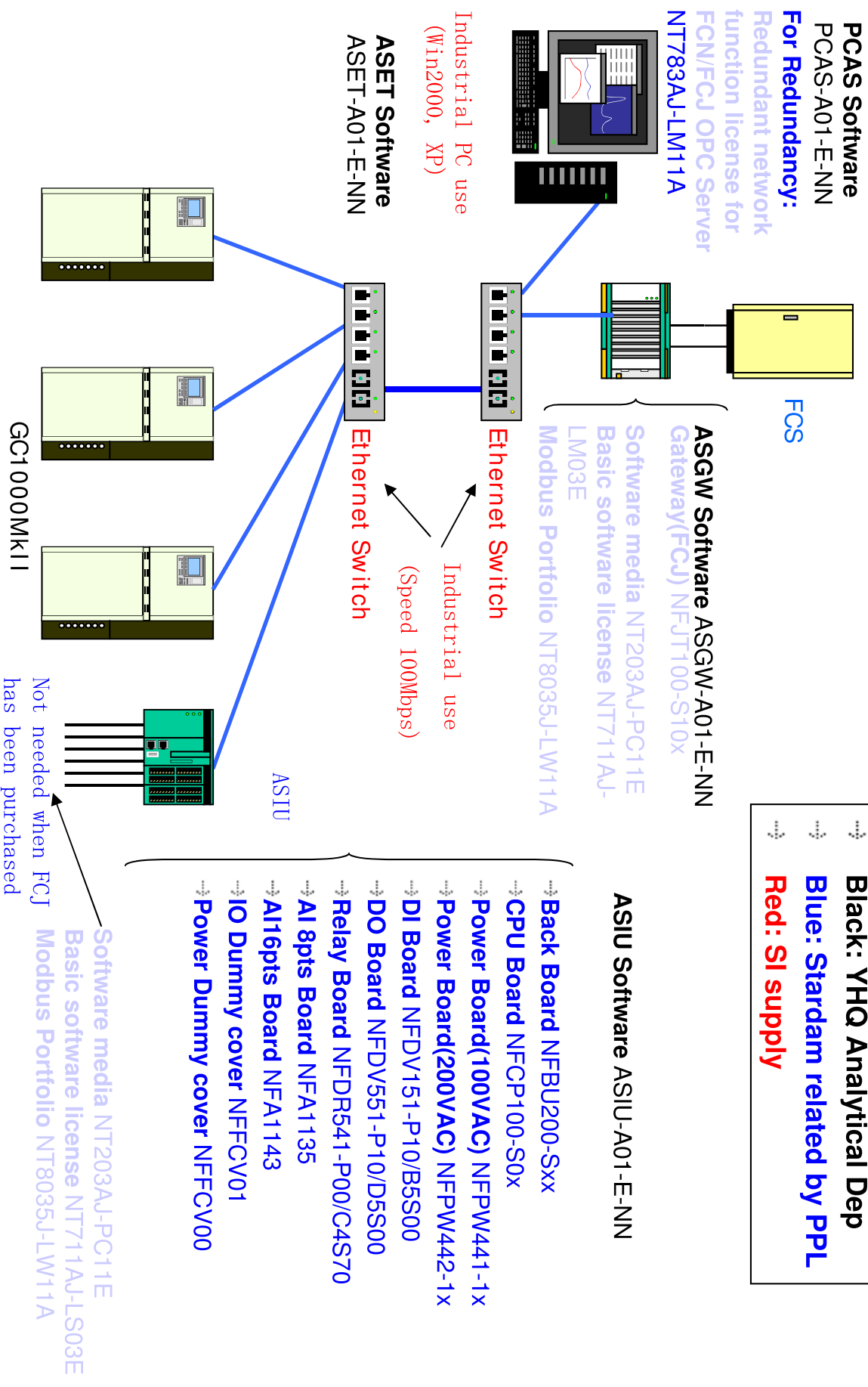
Subject to change
without notice



High Reliability - Redundant system



Supply of Network Components





Problems In GC Troubleshooting

EVALUATING THE PROBLEM:

The first step in any troubleshooting effort is to step back and evaluate the situation. Rushing to solve the problem often results in a critical piece of important information being overlooked or neglected. In addition to the problem, look for any other changes or differences in the chromatogram and the Process. Many problems are accompanied by other symptoms. Retention time shifts, altered baseline noise or drift, or peak shape changes are only a few of the other clues that often point to or narrow the list of possible causes. Finally, make note of any changes or differences involving the sample. Solvents, operation conditions, process age, extraction or preparation techniques, or any other factor influencing the sample environment can be responsible.

There have been reported “broke GCs” that ended up being units monitoring Demethanizer Overheads with the “error” of drift. This drift had a real nice cycle of 12 hours.....any guess the problem.



Problems In GC Troubleshooting

SIMPLE CHECKS AND OBSERVATIONS:

A surprising number of problems involve fairly simple and often overlooked components of the GC system or analysis. Many of these items are transparent in the daily operation of the GC and are often taken for granted (set it and forget it).

1. Gases - pressures, carrier gas average linear velocity, and flow rates (detector, vents, split vent, carriers).
2. Temperatures - column, injector, detector and transfer lines.
3. System parameters - purge activation times, detector attenuation and range, mass ranges, etc.
4. Gas lines and traps - cleanliness, leaks, expiration.
5. Injector consumables - seals, liners, O-rings and ferrules, purges.
6. Sample integrity - concentration, degradation, solvent, storage.
7. Data system - settings and connections.



Problems In GC Troubleshooting

GHOST PEAKS AND CARRYOVER:

System contamination is responsible for most ghost peaks or carryover problems. If the extra ghost peaks are similar in width to the sample peaks (with similar retention times), the contaminants were most likely introduced into the column at the same time as the sample. The extra compounds may be present in the injector (i.e., contamination) or in the sample itself. Impurities in carriers, utilities, and piping are only some of the possible sources. Injecting sample and blanks may help to find possible sources of the contaminants. If the ghost peaks are much broader than the sample peaks, the contaminants were most likely already in the column when the injection was made. These compounds were still in the column when a previous GC run was terminated. They elute during a later run and are often very broad. Sometimes numerous ghost peaks from multiple injections overlap and elute as a hump or blob. This often takes on the appearance of baseline drift or wander.

If you are using a Variable Temperature Oven, increasing the final temperature or time in the temperature program is one method to minimize or eliminate a ghost peak problem.

Alternatively, a short bake-out after each run or series of runs may remove the highly retained compounds from the column before they cause a problem. Performing a condensation test is a good method to determine whether a contaminated injector is the source of the carryover or ghost peaks.

Increase purge times and time between samples as much as possible.

Column Degradation

❖ Column Degradation is a common type of “failure” in GCs.

❖ It can be the result of several things:

- **Column Breakage**
- **Thermal Damage**
- **Oxygen Damage**
- **Chemical Damage**
- **Column Contamination**

Trouble Shooting Analysis

Excessive Baseline Noise

Possible Cause	Solution	Comments
Injector contamination	clean the injector	gas lines may need cleaning
Column contamination	Bake out the column Solvent rinse the column	Limit bake out to 2 hrs. Bonded and cross linked phases only
Detector contamination	clean the detector	noise increases over time, and not suddenly
Contaminated or low quality gases	use better grade gases check for gas leaks and expired gas traps	usually occurs after changing a gas cylinder
Incorrect detector gas flow rates	adjust flow rates to recommended values	consult literature

Leak when using MS, ECD, or TCD	find and eliminate the leak	usually at the column fittings or injector
	replace appropriate part	use new part
Old detector filament, lamp, or multiplier		
Un-equilibrated detector	allow detector to stabilize	may require up to 24 hrs to fully stabilize
Incompletely conditioned column	fully condition column	critical for trace level analyses



Trouble Shooting Analysis

Change in Peak Size

Possible Cause	Solution	Comments
Change in detector response	Check gas flows, temperatures, and settings. Check background level or noise	All peaks may not be equally affected. May be caused by system contamination and not the detector
Co-elution	Change column temperature or stationary phase	Decrease column temperature and check for appearance of a peak shoulder or tail
Change in the purge activation time	Check the purge activation time	For split less injection
Change in the injection volume	Check injection technique	Injection volumes are not linear
Change in sample concentration	Check and verify sample concentration	Sample degradation, variances in sample temperature or pH
Leak in the syringe	Use a different syringe	Sample leaks passed the plunger or around the needle, Leaks are often not readily visible
Column contamination	Trim the column Solvent rinse the column	Remove about half to 1 meter from the front of the column. Only bonded and cross linked phases
Column activity	Irreversible	Only affects active compounds



Trouble Shooting Analysis

Tailing Peaks

Possible Cause	Solution	Comments
Column contamination	Trim the column Solvent rinse the column	Trim half to 1 meter from the front of the column Only for bonded and cross linked phases
Column activity	Irreversible	Only affects active compounds
Solvent-phase polarity mismatch	Change sample solvent Install a retention gap	More tailing for the eluting peaks, or those closest the solvent front 3 to 5 meter retention gap is sufficient
Solvent effect violation for split less or on-column injections	Decrease the initial column temperature	Peak tailing decreases with retention gas lines may need cleaning
Too low of a split-ratio	Increase the split-ratio	Flow from split vent should be 20ml / min or higher
Poor column installation	Reinstall the column	More tailing for the early eluting peaks
Some active compounds always tail	None	Most common for amines and carboxylic acids

Trouble Shooting Analysis

Retention Time Shift

Possible Cause	Solution	Comments
Change in carrier gas velocity	Check gas velocity	All peaks will shift in the same direction by approximately the same amount
Change in column temperature	Check column temperature	Not all peaks will shift by the same amount
Change in column dimension	Verify column identity	Switched column?
Large change in compound concentration	Use a different sample concentration	May also affect adjacent peaks
Leak in the injector	Leak-check the injector	A change in the peak size occurs also
Blockage in gas line	Clean or replace clogged line	Most common for split line. Check flow controllers and solenoids



Trouble Shooting Analysis

Split Peaks

Possible Cause	Solution	Comments
Injection technique	Change technique	Erratic plunger depression or having sample in needle
Mixed sample solvent	Change to single solvent	Worse for solvents with large differences in polarity or boiling points
Poor column installation	Reinstall column in the injector	Usually a large error in the insertion distance
Sample degradation in the injector	Reduce the injector temperature. Change to an on-column injection	Peak broadening or tailing may occur if the temperature is too low Requires an on-column injector




Trouble Shooting Analysis

See the long list



Trouble Shooting Analysis

The GAC oven is NOT a Microwave



2008 User Conference & Technology Fair

THE END

Thank you for your time and patience.
I hope this was informative for you.

Darryl D. Hazlett
Sales Manager GC, FTNIR, and
Analytical Systems
3/27/08