A QUICK Overview : PRACTICAL GUIDE TO CAPILLARY GC

Capillary GC is unique in it's the high separation power and its capabilities of analysing both simple and highly complex mixes.
Applications ranges from gases to high MW high boiling sample from many application fields . . . from petroleum , environmental, forensic, pharmaceutical,
Columns vary from thin film liquid phase columns now almost universally based on highly flexible and potentially inert fused silica.
Recent innovations extend to the use of Siltek deactivation of fused silica and metal components in the GC sample path.
The ultimate columns are now being made of MXT; Siltek deactivated stainless steel from Restek with Siltek deactivation approaching that of the best deactivated fused silica
The Rxi - range of Fused Silica columns from Restek are exceptional in their inertness
Advances have also been made in cross-bonding liquid phase technology to reduce the column bleed and suitability of select phases to high temperature with extended GC/MS applications in minutes
The most universal phase and a starting point for many applications is the Rxi-5 type; 5% phenyldimethyl silixane pahses . . . in 30metre x 0.25mmID with a 0.5um film thickness
A Silphenylene derivative of this in the form of Rxi-5SilMS extends the temperature range and reduces bleed of the Rxi-5MS type even furtther

Selectivity for some applications is offered by a variety of different polarity phases
Rtx-1, Rtx-5, Rtx -20, Rtx-35, Rtx-50, Rtx-440, Rtx-200, Rtx-1301, Rtx-624, Rtx-1701, Rtx-225, Rtx-2330, Rt-2560, Rtx-WAX, Stabilwax
A unique High Temperature 300degC version of CW20M is now available from MEGAColumns301, Rtx-624,
Advance in GC hardware has slowly led to FastGC methodology at last seeing some fruition of this technology originally pioneered some 40 years ago . . . OEM hardware and computers are catching up
Often misconstrued aut used in context offering separations of complex mixtures in minutes often reducing analysis times by a factor of 10 or 20 or more particularly compared to old packed columns
These can for most intents and purposes now be declared obsolete/redundant
Except perhaps here methods have been set in dogma by the works of USP (Pharrmaceuticals and ASTM (petrochemicala) and AOCS(food analysis) where inertia rules.
But even her methodology is open to demonstation of acceptance to equal of better performance overlooked by lazy analysts

ACHIEVMENT OF OPTIMIMUM SEPRATION PERFORMANCE IS NOT WITHOUT ITS CHALLENGES BY GC OEMS BUT MORE-SO ATTENTION TO DETAIL AND UNDERSTANDING OF SOME BASIC PRINCIPLES BY GC END-USERS

1 Attention to low dead-volume issues re connecting tubing Injector to column and column to detector and even to the use of miniDetectors with effective low dead-volume

2 The need for sample prep derivatisation and cleanliness to reduce particulates and matrix effects is all too important but often neglected for expediency.
Simple filtration of samples can minimise contaminations of Injector liner and columns
Use a syringe filter or

- NEW Single-Step Filter Vials or
- SPE Cartridges for sample cleanup
  Aqueous samples by Direct injection should always be avoided except where absolutely necessary or on columns specifically designed for its use polar phase being more problematic
- The use of guard columns (retention gaps) can also prolong column life

3 Restricting Sample size and concentration within limits determined by ID and film thickness
4 At all times keep the on-column injected sample size as small as practical (and consistent with detection limits) Often 0.1ul is adequate and Inlet Split ratios of 50:1 are used.

(Continued from page 1)

5 Avoid the use of Direct On-column injection if at all possible (phase stripping and blocking the column with sample residues but moreso specks of septum material from use of worn septa or blunt syringe needles
Modified injection system for increased sample sizes (PTV and SPME) add to the complexity but enhance limits of detection levels
Injection techniques of Headspace analysis for volatiles in water and solids avoid matrix effects
Liquid Autosampler injection can help sample throughput issues but attention to details re speed of injection, sample size is also important

6 Septa USE HIGH QUALITY Low Bleed Septa - It IS False economy to compromise
Replace Septum regulary 50 to 100 Injection BUT INSPECT the Septa regularly
Inferior Setum can produce bleed effects During in-between injection times this bleed is continuously emitting bleeding from the HOT Injector into the column focusind on the cool front of the column prior to temperature programming.
and Septum Bleed devices only partly minimise this -it IS consequently time dependant
Use a minimal Injector temperature but consistent with sample volatility requirements
Excessive bleed and column peak artifacts are exacerbated by using too large an injected volume
NEVER USE 5uL (which seems to be a standard size and quite useless for Capillary GC) in a standard liner
FLASH BACK occurs absorption/desorption into the septum occurs and also in the body of the injector causing at best solvent tailing effects and associated "ghost" peaks
Matrix solvent are worse in Order Water>MeOH,> MeCl2>Hexane> isooctane sample miscibility often being the determining factor

7 GC Diagnostics

1 With a new GC establish a working "baseline re performance
Insist on a Column performance evaluation by the OEM GC Supplier
Use a new column of guaranteed and individually tested Column Efficiency performance and inertness by using a suitable Column Test mixture (GROB Test Mix)

Table II Typical characteristics for columns with the same phase ratio, such as 0.10 mm ID x 0.10 µm and 0.18 mm ID x 0.18 µm, etc.

	Column ID					
Characteristic	**0.10mm**	**0.15mm**	**0.18mm**	**0.25mm**	**0.32mm**	**0.53mm**
Helium Flow (@ 20cm/sec.)	0.16mL/min.	0.3mL/min.	0.3mL/min.	0.7mL/min.	1.2mL/min.	2.6mL/min.
Hydrogen Flow (@ 40cm/sec.)	0.32mL/min.	0.6mL/min.	0.6mL/min.	1.4mL/min.	2.4mL/min.	5.2mL/min.
Sample Capacity (max load per component)	<10ng	<40ng	<50ng	50–100ng	400–500ng	1000–2000ng
Theoretical Plates/Meter	8000	4000	3500	3200	2500	1800

This has confused many and is often overlooked as being academic perhaps by those so called practical chromatographer many Data Systems (in)convenienly omit this simple calculation or even measure peak widths

It is the perfect measure of the GC System performance
Injector + Column + Detector + DataSystem
but Most DataSystems will NOT perform as well as an old 1sec FS Chart Recorder re speeds
To actually measure w1/2 expanded scales are required to measure capillary peak widths
(of the order of a few seconds)

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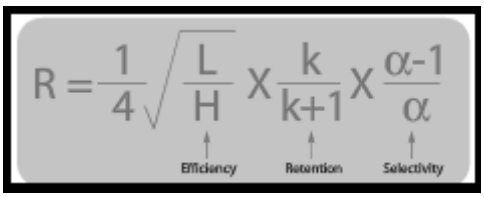

The **Effective Number of Theoretical Plates** is a more meaningful measure of the separation efficiency of any particular column Or GC System

An understanding of this basic formulae is fundamental to chromatography where HETP= L/Nt
Nt=5.54[(tr-ta) / ta]sqd; k=tr-ta/ta t r/ta are retention time of the test peak and the air peak respectively

The interaction of HETP and k is a bit profound and had escaped many GC system analysts/"experts" over the years k
For a given application of course the selectivity factor(Alpha) is a choice from a wide choice of liquid phase polarities

3 The extreme selectivity being molecular shape separation on Chiral phases
But it is also of note the selectivity can be a columns temperature variable

An optimal System should experimentally deliver 90% of the Theoretical Efficiency (Nt)
This is highly dependant on flow rate NOT ml/min but u cm/sec and Helium gives better optimum Efficiency results than H2 whereas the latter is beneficial for FAST GC

3 A GC will not perform adequately with High Resolution columns unless the A/D is 50Hz MINIMUM and for FAST GC 300Hz is recommended . . . *AND THAT'S PER CHANNEL !*
Multi-detectors invariable degrade this performance

Use TOTAL THEORETICAL PLATES Measured Isothermally at the Optimum Flow Velocity
Peak measured must have a Capacity Factor > 5.0 to be realistic
See Restek www.chromalytic.net.au/catalogs/restek#24

Operational Factors

- Never exceed the MAX Recommended Operating Temperature for a specific Column Liquid Phase Type
- Use an **Indicating Oxygen Trap** on the Carrier Gas (as close to the injection port as practicable
  Take care in changing cylinders not to introduce a slug of air into the tubing that will deactivate the Oxytrap
  Thin Films are more stable than thicker; 0.25um in 0.25mmID columns
  A badly designed GCs will make us of flow rotameters and crude pressure regulators which will leak air through rubber O-rings and diaphragms or use Teflon tape as thread seals (useless)
  Pressur Egauges can also be misleading as they can act as exp[onential dilution flask on GCstart up of taking hours to equilibrate and reduce trapped air
- Never run a Columns at >150deg C without carrier gas
- Allow the GC to "warm up" at a low column temperature before doing analytical work
  For PTGC often a blank run is required to desorb any built-up system
  Without an Oxytrap columns detrioration via bleed is observable starting from 150degC even on otherwise normally stable Rtx-5.
  Acceptable bleed on a Rx5-MS column is of the order of 2 to 5 pAmp at 300DegC
- Do NOT Trust High Purity Gas Cylinders fro Gas Suppliers
  They are ONLY tested on a master batch "tank: and don't allow for bottle filling mistakes in production
- Do NOT use plastic tubing for gas lines even PEEK is suspect re air diffusion and organic bleed at high GC sensitivity

3 An alternative method often use is via Separation Number (Trensvaal) applicable for Temperature Programmed GC runs

DO NOT PLACE AN ORDER WITH A GC SUPPLIER WHO IS NOT PREPARED TO PRESENT DATA OR GUARANTEE THIS "DECLARED" INITIAL GC PERFORMANCE

MOST GC OEMS DO NOT DO THIS ! - Buyer Beware !

Use this criteria to assess system deterioration with time and useage

By attrition . . . The following Hints may be useful

IF the Column appears to be a “dud“ after some “system useage “ . . . Either through loss of peak shape, loss of peaks completely or reducted separation performancesystem
DO NOT THROW THE COLUMN OUT
Replace the column with another of proven performance preferably on Alternative GC

First SUSPECT . . .
1 the Injector Liner - check for particulates (septum rubber specs or residues (wash with pure methyl chloride and dry

HINT : NEVER USE A NON-DEACTIVATED GLASS OR WORSE A METAL LINER - It IS False economy
SILTEK DEAVATION BY RESTEK IS UNIVERSAL AND ACCEPTED AS THE CRITERIA FOR INERTNES
Fused Silica is NOT! Necessarily inert

CHROMALYTIC AND SILCOTEK now offer a re-deactivation Service for used Liners
(Any GC make or size with Guaranteed 99+% inertness of a new One !
Done in a batch of 20+ - can be cost effective long term

MXT Or SILTEK Deavtivated SS liners now approach the intertness of SILTEK Glass - unortunately they are opaque and you can’t visibly see any residue contamination if present
2 Suspect the Syringe . . . a blunt needle and even blocked by cored septum material
In cage of gas analysis GasTight syringes are never GasTIght unless warned to over 30degC due to the Teflon tip on the plunger
3 Check the end of the column - must be square cut with no “dags” of polyimide film (from the OD of the Fused Silica) bridging the column hole - USE A MAGNIFYING GLASS TO INSPECT
Grapghite Ferrules are soft and malleable and very effective for positive pressure GC IN/Outlet but NOT recommended for GC/MS Columns outlet - the laminated structure of the Graphite ferrule can lead to in-diffusion of air at trace levels
HOWEVER Care is needed in inserting the ferrule into a column NOT to get a spec of graphite into the column Insert the column though the GF the break off ~10mm of the column to be sure.
Graphite/Polyimide ferrules are a lot harder material and can dry out at high temperature (>280C) and can leak after temperature cycling -It is easy to “crunch” the fused silica IF overtightened

Application Notes
www.chromalytic.net.au/flip/grobtestmix/

GROB Mix to diagnose some GC Problems

Typical Restek Columns Results Test Reports

A “Lit” Application utilising some new Fast GC design specs