

## Observations concerning...

a compound

a matrix

a method

other

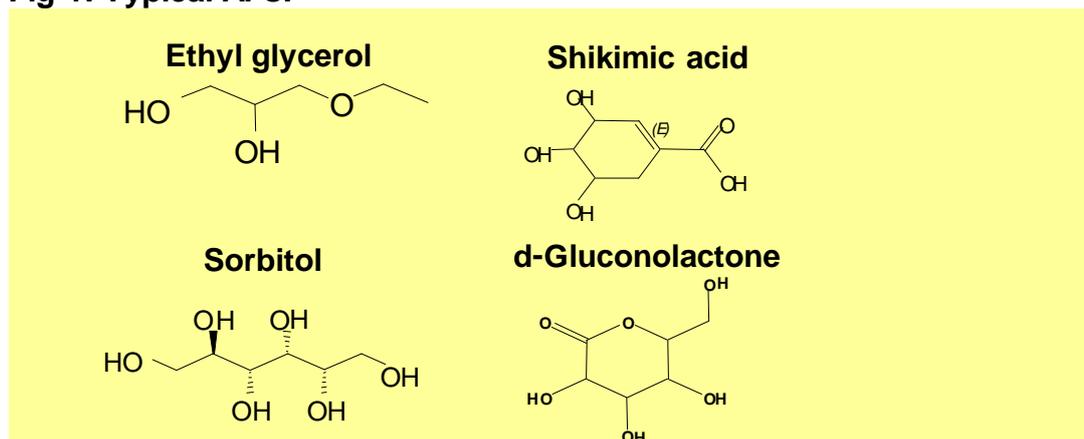
## Use of Analyte Protectants in GC-Analysis a way to improve peak shape and reduce decomposition of susceptible compounds

Reported by: EURL-SRM  
Version 1 (last update: 22.04.2013)

### Brief description of problem/observation/solution:

The GC-analysis of various pesticides is quite problematic due to unwanted tailing and decomposition phenomena. Both phenomena are related to active sites on the surface of the GC-system and become more pronounced the more contaminated the GC-system becomes. Replacing the liner and cutting the first part of the column are only temporary measures as new non-volatile components from the injected extracts are deposited forming new active sites. Analyte protectants (APs) help to reduce analyte tailing and decomposition within the GC-Inlet by masking these active sites. This effect is also called “matrix-induced signal enhancement”. Most effective as APs are compounds entailing multiple hydroxyl-groups with which they can effectively interact with the active sites via hydrogen bonds. To be effective APs have to be added to solutions (e.g. extracts, standard solutions) at concentration by far exceeding those of the analytes to be protected. In many cases the protective effect exhibited by APs is stronger than that of matrix components. With this in mind APs are added to both calibration solutions in solvent and sample extracts to equalize the protective potential, thus obviating the need for matrix-matched calibrations. APs are often employed as a mixture of compounds each covering a different volatility range.

Fig 1: Typical APs:



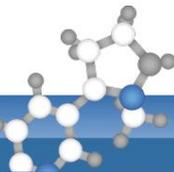


Fig 2: The AP-principle:

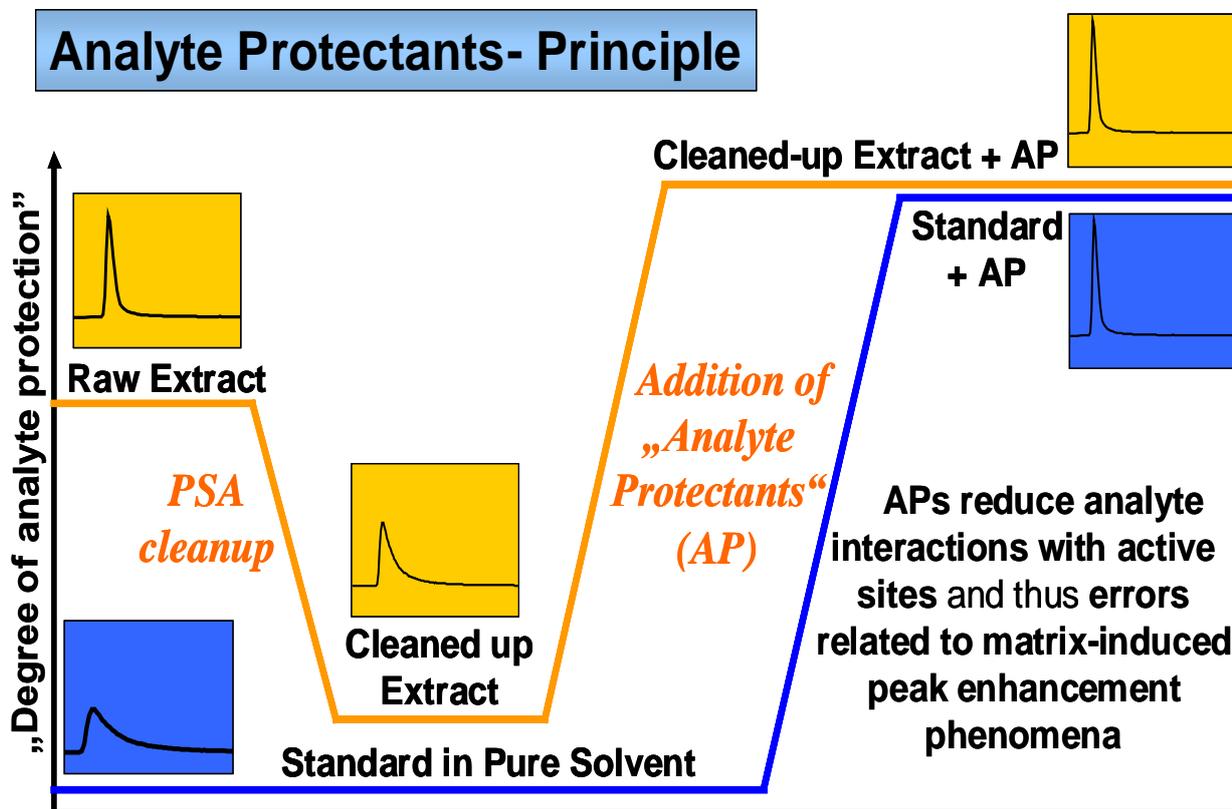
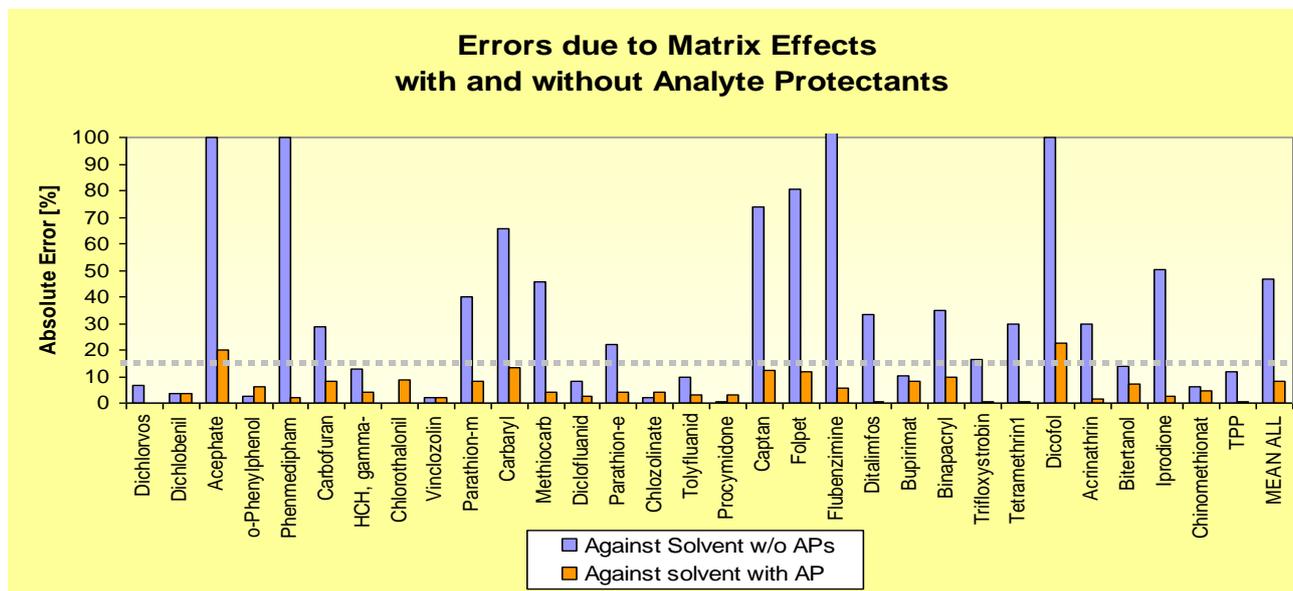
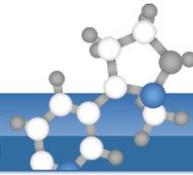


Figure 3: Equalization of matrix effects between a standard in blank extract and a standard in neat solvent by adding APs to both





Copies of slides illustrating the AP-principle

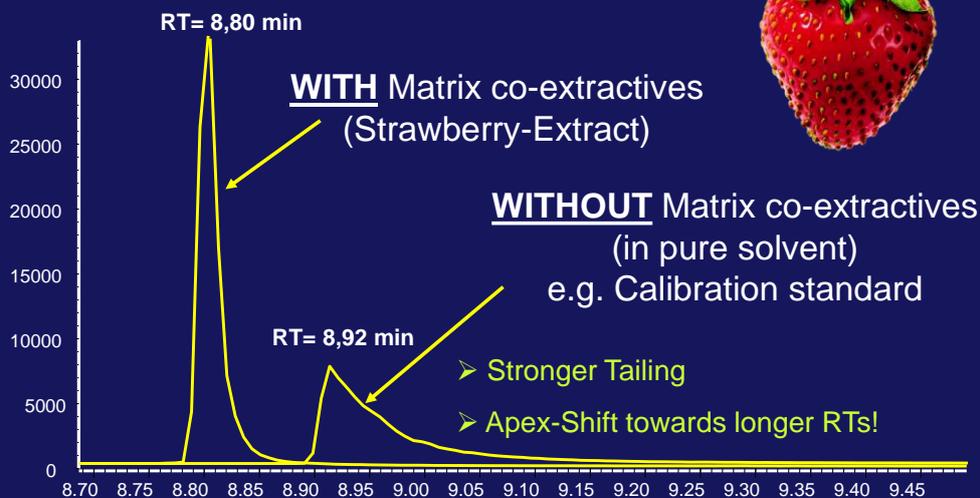
## „Matrix-Induced Peak Enhancement Effect“

**GC-Liner**

**GC-Capillary**

- Active Sites** (on Surface of GC-Liner & Column )  
(Siloxanes & deposited non-volatile matrix-co-extractives)
- Analytes** (interact with Active Sites)
  - Unwanted Retention/Tailing
  - Quasi-catalysed degradation (susceptible compounds)
- Matrix-Components** (in Excess)
  - Bloc active sites and protect analytes

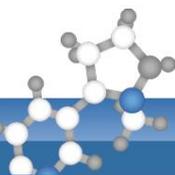
Analyte: **Atrazine** ; Matrix: **Strawberry**



### Ratios:

- Peak-Areas: ~ 1,5:1
- Peak-Heights: ~ 4:1
- Peak-Width (at half height): ~ 1:3

**Matrix-Induced Peak Enhancement**  
⇒ **OVERESTIMATION OF RESULTS!!**


**Instructions for the production and use of an AP-mixture:**

 a) Prepare the solvent:

	Acetonitril content [%-Vol.]	Water content [%-Vol.]
<b>Solvent A</b>	<b>60</b>	<b>40</b>

 b) Prepare AP stock solutions (store at 4°C):

 • **Sorbitol (CAS Number: 50-70-4)**

Sorbitol [mg]	Solvent A [mL]	Concentration of stock solution [mg/mL]
<b>500</b>	<b>10</b>	<b>50</b>

 • **D-(-)Gluconic acid- $\delta$ -lactone (CAS Number: 90-80-2)**

D-(-)Gluconic acid- $\delta$ -lactone [mg]	Solvent A [mL]	Concentration of stock solution [mg/mL]
<b>500</b>	<b>10</b>	<b>50</b>

 • **Shikimic acid (CAS Number: 138-59-0)**

Shikimic acid [mg]	Solvent A [mL]	Concentration of stock solution [mg/mL]
<b>500</b>	<b>10</b>	<b>50</b>

 • **3-Ethoxy-1,2-propanediol (CAS Number: 1874-62-0)**

Use pure substance without dilution.

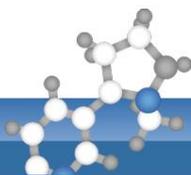
 c) Preparation of AP-Mixture (use volumetric flask)

- 1) Weigh 2 g of 3-Ethoxy-1,2-propanediol in a 10 mL volumetric flask
- 2) Add 2 mL D-(-) Gluconic acid- $\delta$ -lactone stock solution
- 3) Add 1 mL Sorbitol stock solution
- 4) Add 1 mL Shikimic acid stock solution
- 5) Fill the volumetric flask up to 10 mL with solvent A

 d) Spike extracts or standard solutions with AP-mixture

Use 30  $\mu$ L AP-Mix per mL of sample extract or solvent-based calibration solution (30  $\mu$ L/mL).

*Note: Different GC-Systems may require different amounts of APs.*



## AP-Related Publications:

### Papers:

1. M. Anastassiades, K. Maštovská, and S.J. Lehotay *J. Chromatogr. A*, 1015 (2003)\_163-184
2. K. Maštovska, S.J. Lehotay and M. Anastassiades, *Anal Chem* 77 (2005) 8129

### Posters:

1. M. Anastassiades, S. Lehotay, **'Reduction of Analyte Degradation and Peak Tailing During GC Injection by Addition of Protecting Agents'**  
4<sup>th</sup> European Pesticide Residue Workshop in Rome/Italy, Awarded as best Poster
2. M. Anastassiades, E. Scherbaum, B. Tasdelen: **'Investigations on the use of analyte protectants for multiresidue GC analysis'**  
6<sup>th</sup> European Pesticide Residue Workshop in Corfu/Greece