Automated Liner Exchange for GC injectors

The GERSTEL Automated Liner EXchange (ALEX) enables routine GC analysis of samples containing large amounts of matrix or other solid residue. After several injections, matrix material deposited in the GC inlet leads to adsorption and loss of active analytes, such as pesticides. ALEX replaces the GERSTEL CIS inlet liner at user-defined intervals, eliminating the need for time-consuming clean-up steps during sample preparation.

Sample clean-up steps needed to prepare environmental or food samples for determination of pesticides are time-consuming and are potential sources of errors. Simplification or elimination of such procedures is often the motivation for development of new analytical methods and new instrumentation. Unfortunately, analytical instruments do not normally tolerate introduction of "dirty" samples or even "dirty" extracts.

For example, extracts containing suspended matter or high-molecular-weight compounds contaminate a GC inlet after a few injections, causing peak broadening or even loss of sensitive compounds. Reducing or eliminating clean-up steps will result in dirty extracts and daily – or even hourly – maintenance of the GC system.

System Design for Automated Liner Exchange

A simple and automated liner exchange system is able to overcome most chromatographic problems caused by "dirty" samples in GC analysis. A solution is presented that uses a commercially available programmable temperature vaporising (PTV) inlet in combination with an autosampler, which can automatically perform a liner exchange at any time during a sample sequence. Every liner is equipped with a transport adapter, which also allows liquid injection through a septum. Adapters fitted with liners are transported by means of the autosampler which also performs the liquid injection. The system is based on the Cooled Injection System (CIS 4) inlet and the MultiPurpose Sampler (MPS 2) (GERSTEL, Germany). Instead of the septumless head normally used on the CIS 4 for liquid injection, a special support head is mounted. This support head seals the transport adapters, providing an uncompromised carrier gas flow throughthe adapter and liner. The support head and the transport adapters are conical. In order to provide a perfect seal, every transport adapter is fitted with two o-rings, between which the carrier gas inlet is placed. Such a sealing system has been proven through years of use in other systems where glass tubes are automatically exchanged, such as the GERSTEL Thermal Desorption System (TDS).

Figure 1: Automated Liner Exchange (ALEX) installed on an Agilent 7890 GC equipped with a CIS 4 programmed temperature vaporisation (PTV) type inlet. Detailed view of the ALEX System.

In order to grip and transport the adapters, the autosampler has been modified slightly and fitted with an electrical gripper. Up to 97 conditioned liners are stored in a special tray; the transport adapters provide a gas-tight seal for contamination-free storage.

For liquid injections, every transport adapter is equipped with a 5 x 3 mm septum that is commercially available and is, for example, used in Agilent's cool on-column inlet. The top of the injector, and the transport adapter in particular, remain cool during the analysis due to effective heat decoupling between the body and the top of the PTV. As a result, no septum bleeding or bleeding of the o-rings of the adapters can be observed.

Figure 2 Left: Exploded view of transport adapter for automated liner exchange with liner, adapter, 3 x 5mm septum and septum screw; a hole for carrier gas entry can be seen between the o-rings of the transport adapter.
Right: Assembled transport adapter with liner

The body of the injector is identical to the CIS 4 inlet and all commercially available types of liners for this inlet can be used (empty liners or liners filled with glass wool or adsorbents). The automated liner exchange head doesn't affect the analytical performance of the CIS 4 inlet. As an example, Figure 3 shows a chromatogram of a Grob test mixture with uncompromised peak resolution and peak shapes.

Tests with n-alkane mixtures proved that recovery of high boiling substances is comparable to a normal CIS 4 system. It is clearly seen that

- Weigh 10 g of sample **–>** Add 10 ml of Acetonitrile (AcN)
- Shake vigorously 1 min **–>** Add 4 g $MgSO_4$ and 1 gNaCl
- Shake vigorously 1 min **–>** Add internal standard solution
- Shake 30 sec and centrifuge
- Take Aliquot of supernatant **–>** Add $MgSO_4$ and sorbent
- Shake 30 sec and centrifuge
- GC-MS and LC-MS

Table 1: QuEChERS method sample preparation steps for multi-residue analysis of pesticides in non-fatty foods such as fruits and vegetables

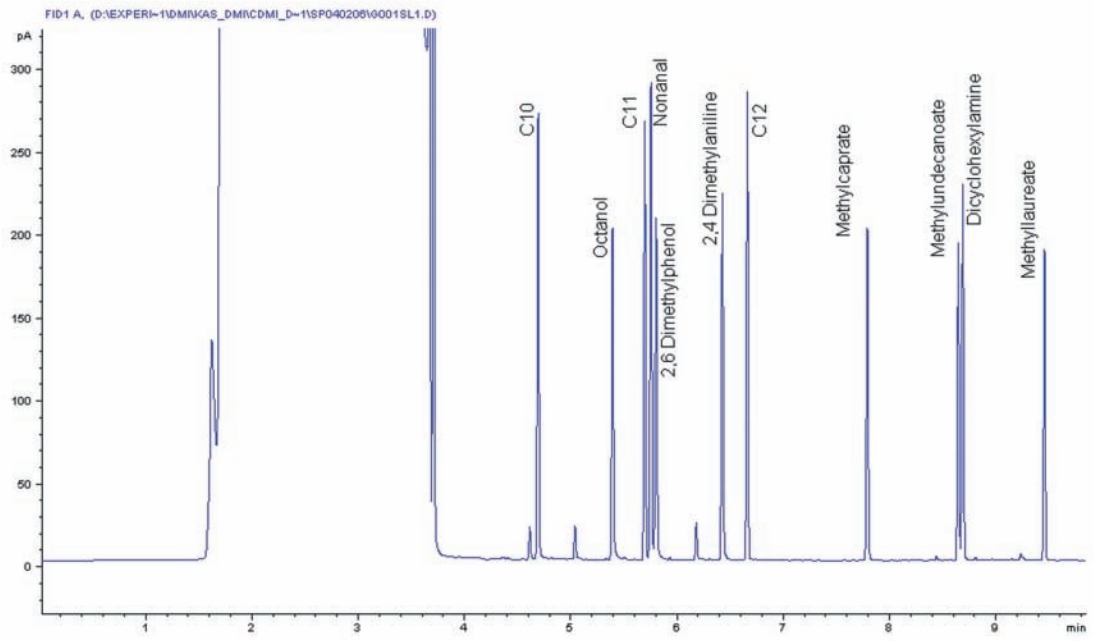

Figure 3: GC FID chromatogram of a Grob test mixture
(1 µL splitless) injected into a CIS 4 equipped with the ALEX system

the Automated Liner EXchange (ALEX) system has no influence on CIS 4 performance. Methods developed for CIS 4 system can be transferred to the ALEX system without any modifications.

A software solution was developed that enables the user to exchange liners at any point in time during the analysis sequence. The software can be operated stand-alone or integrated into the Agilent GC or MS ChemSation. This means that only one sequence list is needed for the complete system. Figure 4 shows a screen shot of such a sample sequence.

Pesticide analysis of non-fatty foods with reduced sample preparation

Recently a new multi-residue method for pesticide analysis in fruits and vegetables was presented (QuEChERS, Quick Easy Cheap Effective Rugged Safe) [1]. Compared to previous methods, the QuEChERS method enables rapid sample preparation for determination of

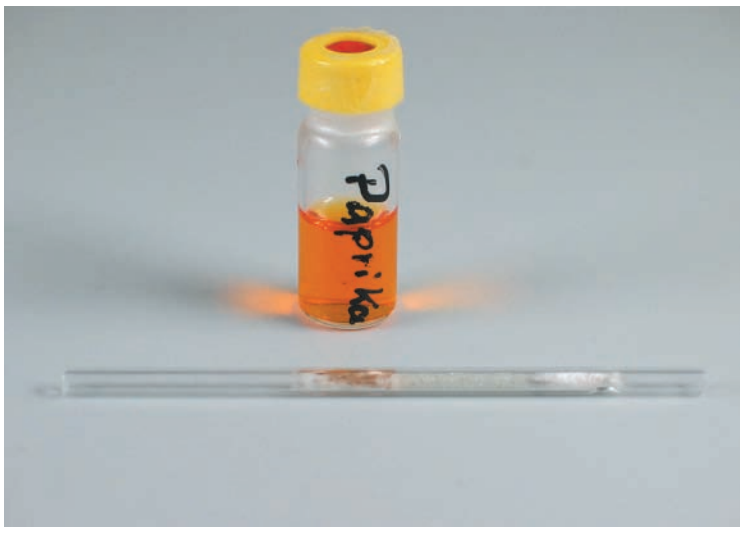

Figure 5: 2 mL Vial containing a QuEChERS method bell pepper extract and a liner packed with glass wool in which 5 µL of this extract has been injected.

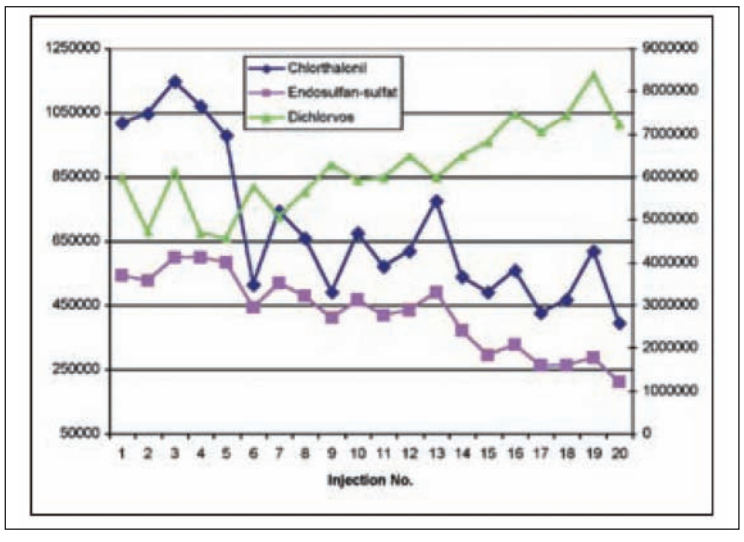

Figure 6: Peak area trend (GC / TOF-MS) for 5 µL injections of a standard solution in matrix (bell pepper) into an empty, deactivated baffled liner

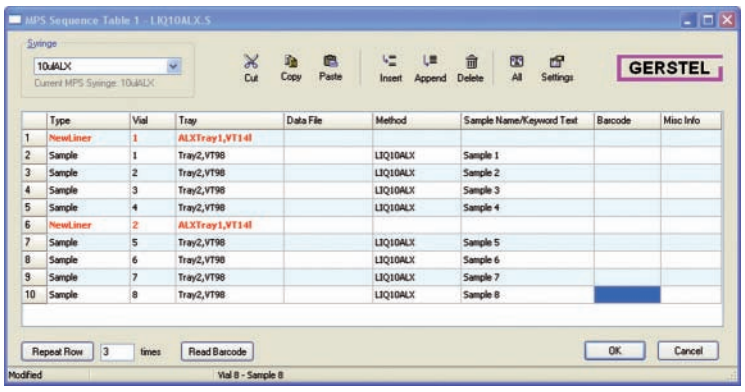

Figure 4: Screen shot of a control sequence for ALEX embedded in Agilent GC ChemStation and MS ChemStation.

pesticides such that 8 samples can be prepared in less than 30 minutes. Table 1 summarises all necessary steps of the QuEChERS method.

The main benefit of this sample preparation method is a less time-consuming analysis, which is also less error-prone. Unfortunately, extracts obtained following this procedure often have a high matrix content, which causes chromatographic problems for GC analysis due to residue build-up in the liner.

Figure 5 shows a picture of a 2 mL vial containing a bell pepper extract and a glass wool packed liner in which 5 µL of this extract has been injected.

Residue build-up in the GC liner very quickly affects the analysis of many pesticides, as can be seen in Figure 6. A 5 µL standard solution made up in a bell pepper matrix was injected 20 times into a deactivated baffled liner. Peak area trends for three different pesticides are presented. For endosulfane sulphate and chlorothalonil, peak areas decrease over the course of the 20 injections. This can be explained with increasing matrix contamination of the liner, leading to loss of analytes. For dichlorophos the situation is different; the peak areas increase. This effect is described in the literature as "matrix-induced chromatographic response enhancement" [2]. This means that matrix components cover remaining active sites in the chromatographic system leading to higher response for sensitive analytes.

Compound	RSD	Compound	RSD
1 Cyhalothrin	9.5%	Imazalil	7.2%
2 Cyhalothrin	6.7%	Cresoxim-methyl	6.7%
Atrazine	9.0%	Methamidophos	6.5%
Azoxystrobin	5.9%	Permethrin	7.0%
Bifenthrin	6.8%	Permethrin 2	6.8%
Carbaril	12.9%	Procymidone	4.7%
Chloropyriphos-methyl	6.9%	Tebuconazol	6.8%
Chlorpyrifos-ethyl	8.5%	Thiabendazole	6.8%
Chlorthalonil	29.3%	Tolylfluanide	8.2%
Cyprodinil	7.7%	Trifluraline	6.9%
Dichlorvos	12.0%	Tritane	3.5%
Endosulfan sulphate	12.7%	o-Phenylphenol	6.8%
Ethion	8.0%	p,p'-DDD	6.1%

Table 2: Standard deviations for different pesticides achieved under optimised injection conditions (see Table 3) for 10 injections in one liner. Even though only 10 injections per liner are performed, relative standard deviations are still high for several pesticides. Apart from the specific chemistry of some pesticides, this is due to the fact that 5 µL of the acetonitrile extract had to be injected into an empty liner. Acetonitrile is known not to be a suitable solvent for GC analysis. Normally for such a solution, and such an injection volume, a liner with glass wool should be used. Unfortunately, some substances are very sensitive and show discrimination on glass wool liners. On the other hand a 5 µL injection volume is necessary in order to meet required detection limits of 0.01 mg/kg.

Figure 6 shows clearly that when analysing extracts obtained with the QuEChERS method, a liner exchange is required after 10 or at least 15 runs for vegetables like bell peppers. In order to implement the QuEChERS method in a laboratory for a routine automated analysis, it is absolutely necessary to have the capability of exchanging liners automatically as is provided by the GERSTEL ALEX system.

Liner	Empty baffled liner (deactivated)
Injection Volume	5 µL (AcN solutions)
Injection Speed	10 µL/sec
Injection Mode	Solvent vent for 15 sec (50 mL/min; 8.2 psi), Splitless sample transfer, Purge Flow 50 mL/min @ 150 sec
CIS 4 Temp. Program	50°C (0.25 min) - 12°C/sec – 280°C (30 min)

Table 3: Injection conditions for Pesticide Analysis after QuEChERS sample extraction method, GERSTEL MPS 2 with ALEX system, GERSTEL CIS 4, Agilent 6890 GC, Varian FactorFour XMS column (30 m, 0.25 mm ID, 0.25 µm film), Leco Pegasus 3 TOF-MS; Liner: Empty baffled liner, deactivated.

The following is an example of a sequence for routine analysis:

1 Liner Exchange

2 Standard Injections for recalibration

(3 or 5 concentration levels)

3 Sample Injections (7 up to 10 runs)

4 Liner Exchange

5 ..Steps 2-4 are repeated.

Conclusions

The system described herein for automatic exchange of PTV inlet liners enables automated GC analysis of samples or extracts with a high content of high boiling substances or suspended matter.

The chosen application, determining pesticides in fruits and vegetables with QuEChERS sample preparation, demonstrates that a reduction of sample preparation steps combined with a GC system which tolerates injection of solutions with a high matrix content is a powerful solution. Laboratory time for sample preparation is reduced dramatically and at the same time a high sample throughput for the analytical instrument is ensured.

References

[1] M. Anastassiades, S. Lehotay, D. Stajnbaher and F. Schenck: Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce. J AOAC Int 86(2) (2003) 412-31.

[2] M. Anastassiades, K. Mastovska, S.J. Lehotay: Evaluation of analyte protectants to improve gas chromatographic analysis of pesticides. J. Chromatogr. A 1015 (2003) 163-184

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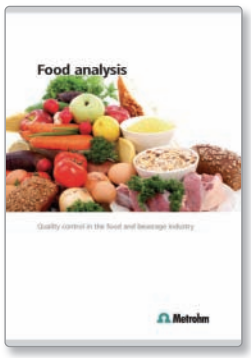
New Metrohm Food Analysis Brochure and Webpage



Numerous parameters define the quality of food and beverage products. **Metrohm's** new brochure «Food analysis» is a summary of the most important of these quality parameters and the methods used to check them. Metrohm's complete know-how (instrumentation and applications) on the analysis of foodstuffs and beverages is also accessible on the web page food.metrohm.com

«Food analysis», which can be ordered free of charge, draws on Metrohm's comprehensive expertise in assuring the quality of food and beverage products. Based on official standards of authorities such as the U.S. EPA, the AOAC and the SLMB, «Food analysis» suggests methods as well as instrumentation best suited to check crucial parameters such as water content, pH value and acidity, oxidation stability, biogenic amines, mono-, di-, oligo- and polysaccharides, free and total sulphurous acid, heavy metals, free fatty acids, to name but a few.

Methods covered include pH measurement, potentiometric, colorimetric, thermometric and Karl Fischer titration, ion chromatography, voltammetry, stability measurement, atline and online process analysis. Solutions for automation in food analysis are presented, too. «Food analysis» is an invaluable tool for anyone who is involved in the professional quality assurance in the food and beverage industry.

The easiest way to access Metrohm's complete know-how on food analysis is a click on food.metrohm.com. Downloads are free of charge.

New Triple Quadrupole GC/MS Offers Greater Precision, Selectivity and Sensitivity

Agilent Technologies (USA) introduce the 7000B Triple Quadrupole Gas Chromatograph/Mass Spectrometer (GC/MS/MS), delivering high confidence in ultra-trace level results, while shortening analysis times for target compounds in complex samples.

The Agilent 7000B provides femtogram-level sensitivity for analyses such as pesticides, PAHs, PCBs, pyrethroids, THC, and steroids in food, environmental, pharmaceutical, and forensic matrices.

Agilent introduced the "A" version of this instrument in June 2008. The 7000 Series system was the first MS/MS specifically designed to handle the rigorous demands of high-temperature separations of complex matrices. Agilent's gold-plated quartz, hyperbolic quadrupole analysers operate at temperatures up to 200 degrees Celsius without any loss of resolution or sensitivity. The 7000B extends the performance and capabilities with the introduction of more sensitive electron ionization (EI) source and a new chemical ionization (CI) source. All of these improvements are reverse compatible to the 7000A.

"With the 7000B introduction, Agilent is shifting the performance emphasis from signal-to-noise to precision." said Terry Sheehan, Ph.D., Agilent GC/MS product manager. "As MS/MS baseline noise approaches zero, RSD of peak response is a far better benchmark of performance. We've designed the Agilent 7000B GC/MS/MS to deliver the precision needed to make accurate qualitative and quantitative decisions even at dwell times as small as 1 millisecond."

The new high-sensitivity EI source sends more precursor ions to the mass analyser, increasing sensitivity and precision. Source temperature is programmable up to 350 degrees Celsius to accommodate complex matrices. High temperature also means less cleaning, reducing labour requirements and increasing uptime. The source is fabricated of solid inert materials, rather than coated, for durability and stable performance.

The new positive and negative CI source generates ideal precursor ions for MS/MS. Based on the proven CI source of the single quadrupole Agilent 5975C GC/MSD, this PCI/NCI source is built to deliver high sensitivity and trouble-free CI operation.

The 7000B MS/MS achieves ultra-fast multiple reaction monitoring (MRM) speed of 500 per second without any "cross talk" between consecutive transitions. High-speed MRM enables users to determine more compounds per ion group than with comparable instruments.

Agilent has enhanced the capabilities of the 7890 GC with a new multi-mode inlet (splitless, PTV and split) and new high-efficiency backflush tools. As compared to traditional column bakeout, backflushing high-boiling matrix extends column life, shortens analysis time, and reduces source maintenance.