Automated Liner-Exchange for GC-Injectors - New Concepts for Handling Dirty Samples

Eike Kleine-Benne, Dirk Bremer, Bernd Rose, Andreas Hoffmann
Gerstel GmbH & Co.KG, Eberhard-Gerstel-Platz 1, D-45473 Mülheim an der Ruhr, Germany

Volkmar Heinke, Karsten Kuhr
Eurofins - Dr. Specht & Partner GmbH, Grossmoorbogen 25, D-21079 Hamburg, Germany

KEYWORDS
Gas Chromatography, Injector, PTV, Automated Liner Exchange, Sample Preparation, Sample Clean-up, Large Volume Injection (LVI).

INTRODUCTION
Sample clean-up steps, which are needed in order to prepare for example environmental or food samples for pesticide analysis, are time-consuming and a potential source of errors. Simplification - or elimination - of such procedures is often the motivation behind the development of new analytical methods and new instrumentation. Unfortunately, analytical instruments normally do not tolerate introduction of “dirty” samples or even “dirty” extracts. For example, extracts containing suspended matter or high-molecular-weight compounds contaminate a GC inlet within 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.
**INSTRUMENTATION**

*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 PTV-injector 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 CIS-4 PTV injector and the MPS-2 autosampler (GERSTEL, Germany). Instead of the septumless head which is normally used with the CIS-4 for liquid injections, a special support head is mounted. This support head seals the transport adapters providing an uncompromised carrier gas flow through the 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 over years in other systems where glass tubes are automatically exchanged, such as the GERSTEL Thermal Desorption System (TDS). 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, where the transport adapters provide gastight seal for contamination-free storage.

![Figure 1. A. ALEX Automated Liner Exchange System installed on an Agilent GC 6890 equipped with a CIS-4 programmed temperature vaporization (PTV) injector (1), ALEX support head mounted on CIS-4 (2), transport adapters for PTV liners with septum (3), electrical gripper for transport adapters (4), Tray for storage of up to 97 fresh and old liners (5), autosampler tower with liquid syringe (6). B. Detailed view on ALEX Automated Liner Exchange System](image-url)
For liquid injections every transport adapter is equipped with a typical 5x3 mm septum that is commercially available and is for example used in Agilent’s cool on-column inlet. The top of the injector, especially the transport adapter, stays cool during usage because of an 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.

Since the body of the injector is identical to the GERSTEL CIS 4 PTV Inlet all commercially available types of liners for this PTV may be used, as there are 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 usual peak resolution and peak shapes for such a test mixture. Test with n-alkanes mixtures proofed that the behaviour of high boiling substances is also comparable to a normal PTV system. Obviously this new automated liner exchange system has no influence on the PTV principle itself. This is an important result. It allows transfer of methods developed previously for a CIS 4 system to the automated line exchange system without any modifications.

Figure 2. Left: Exploded view of transport adapters for automated liner exchange with liner (1), adapter (2), 3x5mm septum (3) and septum screw (4); between the o-rings of the transport adapter a hole for carrier gas inlet (5) can be seen. Right: mounted transport adapter with liner.

Figure 3. GC FID chromatogram of a Grob test mixture (1 μL splitless) injected into a CIS 4 equipped with the automated liner exchange system.

1 Decane
2 Octanol
3 Undecane
4 Nonanal
5 2,6-Dimethyl phenol
6 2,4-Dimethyl aniline
7 Dodecane
8 Methyl decanoate
9 Methyl undecanoate
10 Dicyclohexyl amine
11 Methyl dodecanoate
A software solution was developed, which enables the user to exchange liners at any point in time during a sample sequence. The software is running in stand-alone-mode or is integrated into the Agilent Chemation or MSD Chemstation. This means that just one sample sequence has to be edited. Figure 4 shows a corresponding screenshot of such a sample sequence.

**Figure 4.** Screen Shot of Sequence Control for automated Liner Exchange embedded in Agilent GC-ChemStation and MSD-Chemstation; In this example the sequence starts with a liner exchange, afterwards liquid injections from vial 1 to 10 are performed; After these 10 sample injections the liner will be exchanged and the system is ready for the next 10 sample injections from vial 11 to 20.

**Experimental**

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]. In comparison to normally used methods the QuEChERS-method allows rapid sample preparation for determination of pesticides, 8 samples in less than 30 minutes. The procedure of QuEChERS-method for sample preparation of non-fatty foods like fruits and vegetables for multi residue analysis of pesticides is as follows:

- Weigh 10 g of sample
- Add 10 ml of Acetonitrile (AcN)
- Shake vigorously 1 min
- Add 4 g MgSO₄ and 1 g NaCl
- Shake vigorously 1 min
- Add internal standard solution
- Shake 30 sec and centrifuge
- Take aliquot of supernatant
- Add MgSO₄ and sorbent
- Shake 30 sec and centrifuge
- GC-MS and LC-MS
The main benefit of this sample preparation method is a less time consuming and a less error-prone analysis. Unfortunately extracts obtained following this procedure often contain a high content of matrix that cause the chromatographic problems for GC-analysis as described above due to liner contamination. 

Figure 5 shows a picture of a 2 mL Vial containing a bell pepper extract and a glass wool liner in which 5 μL of this extract were injected only once. Obviously liner contamination arises very quickly which affects the analysis for many pesticides as it can be seen from figure 6. Here 20 injections with 5 μL of a standard solution in bell pepper matrix in one baffled empty liner (deactivated) was done. Peak area trend of three different pesticides is presented. For endosulfan-sulfat and chlorthalonil peak areas decrease within this sequence. This can be explained with increasing matrix contamination of the liner that leads to this substance loss. For dichlorphos the situation is different, its peak areas increase within the sequence. This effect is described in 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.

![Figure 5. 2mL Vial containing a bell pepper extract following the QuE-ChERS-method and a glass wool liner in which 5 μL of this extract were injected only once.](image)

![Figure 6. Peak Area Trend (GC / TOF-MS) for 5 μL Injections of a Standard Solution in Matrix (bell pepper) into one empty and baffled liner (deactivated).](image)
Figure 6 shows clearly that for analyzing extracts obtained with this QuEChERS-method a liner exchange is required after 10 or at least 15 runs for problematic vegetables like bell pepper. This means for implementation of this QuEChERS-method in a laboratory on a routine basis it is absolutely necessary to have the possibility to exchange liners automatically for example by means of the new Automated Liner Exchange System described above. Otherwise a reasonable sample throughput is not possible. Sequences for routine analysis could look as follows:

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. …

Table 1 lists standard deviations for different pesticides that can be achieved with optimized injection conditions (see table 2) for 10 injections in one liner. Even though only 10 injections in one liner are performed standard deviations are still high for several pesticides. Beside the specific chemistry of some of these 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 5 μL injection volume is at least necessary to meet required detection limits of 0,01 mg/kg (related to sample weight).

Table 1. Standard Deviation of Peak Areas for 10 Injections (5 μL) of Matrix-Standard in one Liner.

<table>
<thead>
<tr>
<th>Compound</th>
<th>SD</th>
<th>Compound</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyhalothrin</td>
<td>9,5%</td>
<td>Imazalil</td>
<td>7,2%</td>
</tr>
<tr>
<td>Cyhalothrin</td>
<td>6,7%</td>
<td>Kresoxim-methyl</td>
<td>6,7%</td>
</tr>
<tr>
<td>Atrazine</td>
<td>9,0%</td>
<td>Methamidophos</td>
<td>6,5%</td>
</tr>
<tr>
<td>Azoxystrobin</td>
<td>5,9%</td>
<td>Permethrin</td>
<td>7,0%</td>
</tr>
<tr>
<td>Bifenthrin</td>
<td>6,8%</td>
<td>Permethrin:2</td>
<td>6,8%</td>
</tr>
<tr>
<td>Carbaril</td>
<td>12,9%</td>
<td>Procymidon</td>
<td>4,7%</td>
</tr>
<tr>
<td>Chloropyriphos-methyl</td>
<td>6,9%</td>
<td>Tebuconazol</td>
<td>6,8%</td>
</tr>
<tr>
<td>Chlorpyrifos-ethyl</td>
<td>8,5%</td>
<td>Thiabendazol</td>
<td>6,8%</td>
</tr>
<tr>
<td>Chlorthalonil</td>
<td>29,3%</td>
<td>Tolyllfluamide</td>
<td>8,2%</td>
</tr>
<tr>
<td>Cyprodinil</td>
<td>7,7%</td>
<td>Trifluralin</td>
<td>6,9%</td>
</tr>
<tr>
<td>Dichlorvos</td>
<td>12,0%</td>
<td>Tritan</td>
<td>3,5%</td>
</tr>
<tr>
<td>Endosulfan-sulfat</td>
<td>12,7%</td>
<td>α-Phenylphenol</td>
<td>6,8%</td>
</tr>
<tr>
<td>Ethion</td>
<td>8,0%</td>
<td>p,p'−DDD</td>
<td>6,1%</td>
</tr>
</tbody>
</table>

Table 2. Injection conditions for Pesticide Analysis after QuEChERS sample extraction method, GERSTEL MPS 2 with Automated Liner Exchange System, GERSTEL Cooled Injection System CIS 4, Agilent 6890 GC, Varian FactorFour XMS column (30m, 0,25mm ID, 0,25μm film), Leco Pegasus 3 TOF-MS.

<table>
<thead>
<tr>
<th>Injection conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liner Type:</td>
</tr>
<tr>
<td>Injection Volume:</td>
</tr>
<tr>
<td>Injection Speed:</td>
</tr>
<tr>
<td>Injection Mode:</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Purge Flow 50 mL/min @ 150 sec</td>
</tr>
<tr>
<td>PTV Temp. Program:</td>
</tr>
</tbody>
</table>

TN/2004/01 - 6
CONCLUSIONS
The presented system for automatically changing a PTV inlet liner allows GC analysis of samples or extracts with a high content of high boiling substances or suspended matter on a routine bases. The chosen application, analyzing pesticides in fruits and vegetables with QuEChERS sample preparation, demonstrates that a reduction of sample preparation steps in conjunction with an GC system that tolerates injection of solutions with a high content of matrix compounds is a powerful tool. Laboratory time for sample preparation is reduced dramatically and at the same time a high sample throughput for the analytical instrument is ensured because manual system maintenance remains on usual level.

REFERENCES