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APPLICATION BOOK GC/GCMS

Shimadzu Deutschland GmbH
Albert-Hahn-Str. 6-10
47269 Duisburg · Germany
Tel: + 49 - (0)203 - 7687-0
Fax: + 49 - (0)203 - 7687-680
Email: shimadzu@shimadzu.de
www.shimadzu.de

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Chromatography Volume 1

APPLICATION BOOK GC/GCMS

Content

DRUG AND CLINICAL ANALYSIS

GCMS in drug screening and clinical chemistry 9
TLC/MS offline coupling 10
Higher speed through Fast-GCMS 11

ENVIRONMENTAL ANALYSIS

Determination of oil in water according to DIN H53 14
BETX in water and aldehydes determination in printed colours 16
Super fast and sensitive 18
GCMS helps to chemical disarmament 20
It's quantity that matters 22

ENVIRONMENTAL HYGIENE

"Poison in textiles" 26
Tank up in the rapeseed fields 28
Something in the air 32

FOOD ANALYSIS

Development of a fully automated GC-GC system 36
16 times faster with the GC-2010 38
Fast-GC-ECD analysis of organochlorine pesticides 40
Fruits, not only sweet 43
Customized solutions for complex GCMS problems 46

INSTRUMENTATION

One more success story 50
Innovative design for the highest demands 51
Handy helper for GC and GCMS 52
Cooled PTV injector Optic 3 53
E^3-Concept: Efficient, Excellent, Easy 54

POLYMER ANALYSIS

Not just clean – but pure... 58
All inclusive 60
Saving time in Pyrolysis-GCMS 61
Py-GCMS in polymer and additive analysis 62

SOFTWARE

LabSolutions – Solutions for your laboratory 64
One for all – All for one 65
Automation utilising LabSolutions software 66
Excel lends a hand to improve reports 68
Automated workflow with MS Excel 70
Don't panic 72

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Shimadzu Deutschland GmbH
Albert-Hahn-Str. 6-10 · 47269 Duisburg
Telefon: +49 (0) 203 7687-0
Telefax: +49 (0) 203 766625
Email: shimadzu@shimadzu.de
Internet: www.shimadzu.de

Editorial Team:
Uta Steeger
Telefon: +49 (0) 203 7687-410
Ralf Weber, Adlene Berg

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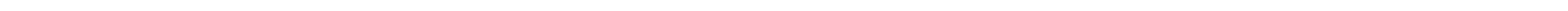
Drug and Clinical Analysis



GCMS in drug screening and clinical chemistry

They look like sweets. Some are stamped with dinosaurs, others with the Olympic Rings, but the innocuous looks are deceiving: drug cocktails are becoming more and more dangerous. They cost the lives of 14 people in Germany in the first nine months of 1996. Private and public interest has particularly focused on such party drugs as Ecstasy. Thousands of young people swallow these feel-good concoctions to make it through allnight techno raves. The possible effects are dehydration and uncontrolled spasms that can lead to cardiac arrest.

The police currently regard labs in the Netherlands as the largest producers and distributors of designer drugs. No one can guess how much ecstasy is brewed and mixed from chemicals in barns, campers and backyards. The growing number of reported incidences would seem to point to the fact that more and more underground labs are producing drug cocktails whose longterm effects (such as Alzheimer's or Parkinson's) cannot yet be estimated. Shimadzu has long been active in the drug analysis field and in the development of high-performance analysis instruments for clinical chemistry. The common analytical factor in these fields is that the samples are human body fluid (blood, serum or urine).

GCMS – For meaningful results

In addition to the long-established, immunological quick screening methods, GCMS technology has taken on firm hold in drug-screening and clinical labs owing to its superior performance and excellent information value.

The range of test applications in drug-screening reaches from classical drugs such as THC (hashish), opiates and LSD to the abusive use of medication such as barbiturates, benzodiazepine, antiepileptic agents and sniffed drugs like poppers.

The reliable answer in doping cases

Of course, a role is also played by doping – the use of anabolic steroids mainly or other steroid hormones by athletes. In this case as well, GCMS technology can find the traces left by these drugs. Note that not only humans keep fit using these illegal methods: horses are also doped to bring them up to performance levels that can be life threatening.

Let's stick to human athletes though. GCMS is used in clinical and therapeutic applications to determine the concentration of steroid hormones or other medications. Potential users are lab doctors and hospitals, as well as forensic scientists and scientists in private institutes. It goes without saying that the police and customs agents are also greatly interested in this technology. In many cases, the substances cannot be determined directly and the samples must be pretreated before GCMS analysis. This usually involves an analysis-specific extraction or derivatization. Shimadzu can guarantee meanwhile the transfer of information in all areas of application over its reference customers.

The current state of development

You can now even read about the current state of technological development. Wiley-VCH have published a book called "GCMS in clinical chemistry". The simple and practical descriptions of current subjects in clinical analysis and the pertinent accompanying information help to put the applications in context and show the practical uses. In addition, there are examples of quality control models for the lab and tips are given on pretreating samples.

- GCMS shows high performance and excellent information in drug screening
- Wide range of drug screening
- GCMS traces doping drugs as well

TLC/MS offline coupling

GCMS-QP2010 with autosampler AOC-5000

- Mass spectrometry provides fast and reliable confirmation
- The GCMS-QP2010 obtains fast results
- The direct-sample inlet DI-2010 is effective in clinical, pharmaceutical and industrial applications

Thin layer chromatography is used in many areas of modern analysis as a screening method. In order to evaluate and to confirm positive results, complementary methods are often needed, particularly in the clinical laboratory. Additional sample preparation is labour intensive and takes up a great deal of time. Therefore, reliable and fast confirmation methods are sought after.

Mass spectrometry provides the required reliable analytical results. Direct-sample introduction MS represents a fast and reliable method for validation. The GCMS-QP2010 system can be equipped with a direct-sample inlet interface (DI-2010) for the introduction of TLC sample fractions.

The advantage of this system is its simple maintenance and the speed with which the results are obtained. A small amount of the selected sample spots on the TLC plate is scratched off and placed on the tile of the direct-inlet sample probe. The sample is thereby directly introduced in the mass spectrometer, heated and evaporated in the ionisation chamber and measured. The resulting thermogram allows an instant check of the TLC screening results within a very short period of time. As the direct-sample inlet is situated at the front of the GCMS-QP2010, it is possible to simultaneously install a GC column. This feature offers the user great flexibility of the system without unnecessary down time due to reconfiguration. The use of the direct-sample inlet is not only limited to clinical chemistry. Wherever TLC is used as a screening method and mass spectrometric confirmation of the results is needed, direct-sample introduction is effective. Another classical application for the DI is the analysis of solid matter. In the pharmaceutical or polymer industry, similar applications as the one described above are conceivable.

QP2010 with direct inlet

Higher speed through Fast-GCMS

Improvements in GCMS as well as in column technology have opened laboratory doors to Fast-GCMS. Due to the reduction in analysis times, short high-performance columns with a small internal diameter can markedly increase sample throughput.

Important in this respect is the use of capillary columns with a maximum internal diameter of 0.1 mm. As the separation efficiency of a column is inversely proportional to its internal diameter, the capillaries can be distinctly shorter, in order to solve a particular separation problem. Consequently, the analysis time is markedly reduced without loss in resolution.

The requirements of the GCMS system for fast chromatography are extremely diverse. On the one hand, the use of high carrier gas pressures in the range of 4 - 9 bar must be possible to attain an optimal linear carrier gas velocity. On the other hand, the split ratio is usually higher than for conventional capillary columns, because the shorter columns have a higher sample capacity. Both of these requirements are met using the GC-2010 incorporated in the GCMS-QP2010 with pressures up to 970 kPa, flow up to 1200 mL/min and the constant linear velocity mode for highest resolution.

As peaks are considerably narrower due to the shorter retention times, fast data acquisition, meaning: a fast scan rate, becomes essential. With a maximum scan rate of 10,000 amu/s the GCMS-QP2010 can run up to 50 scans per sec., depending on the scanned mass range. The GC-2010 features a fast oven-heating rate, fast cool-down time as well as carrier gas pressure programming with constant linear velocity mode which are indispensable for this fast analytical technology.

The impressive improvement in productivity (more samples in a shorter time) can be demonstrated in the following example of Fast-GCMS analysis in the area of drug screening.

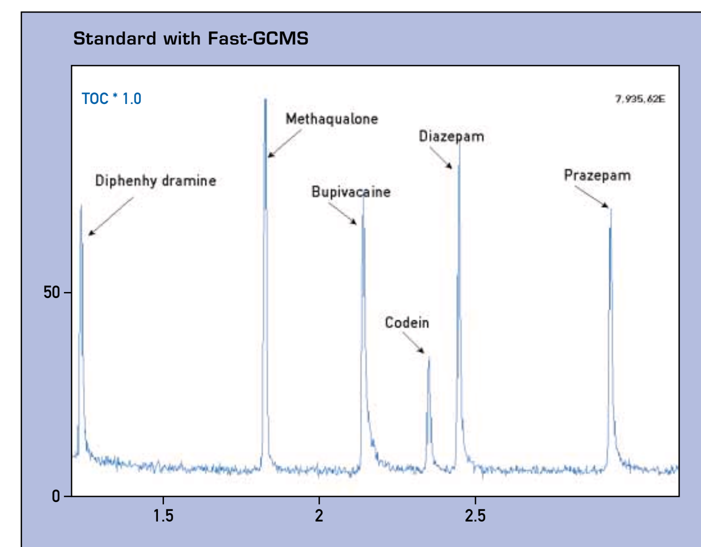


Figure 1 shows the chromatogram of a drug standard with Fast-GCMS

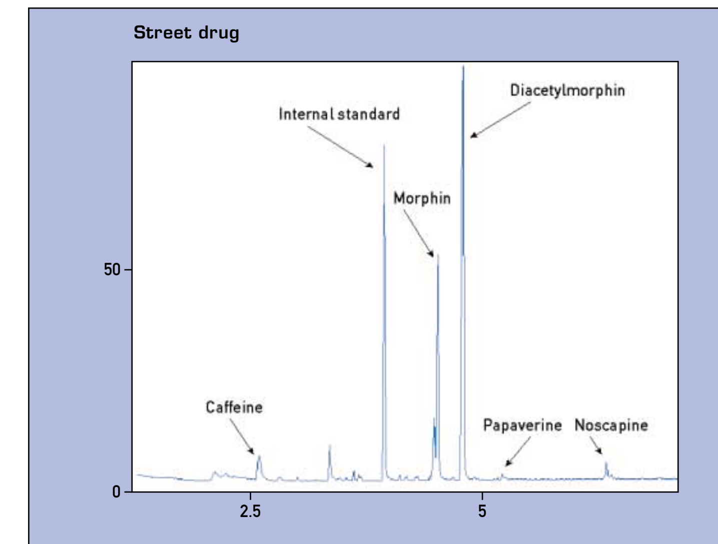


Figure 2 shows the chromatogram of a street drug. The analysis time is 7.5 min, in order to be able to determine both papaverin and noscapin

- Short high-performance columns increase sample throughput
- The analysis time is reduced without loss in resolution
- Impressive improvement in productivity

Environmental Analysis

Determination of oil in water according to DIN H53

Fast, faster, "Fast-GC"

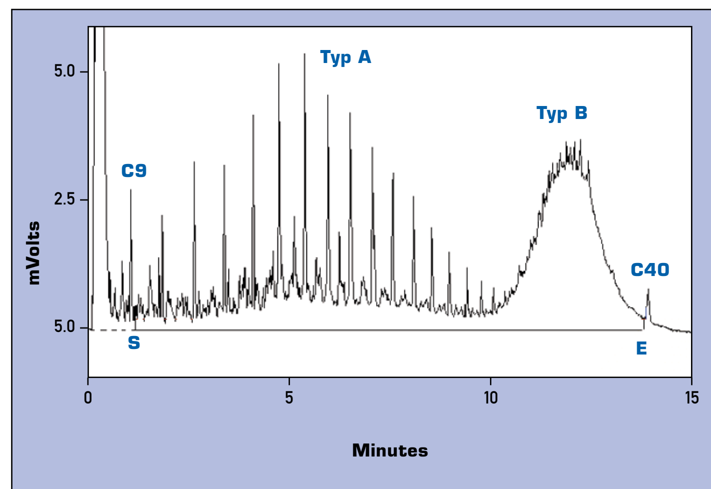


Figure 1: Chromatogram of a calibration mixture containing diesel and lubricating oil (0.8 mg/mL) dissolved in cyclohexane. n-Nonane and n-tetracontane were added to the solvent for determination of the integration limits (S and E)

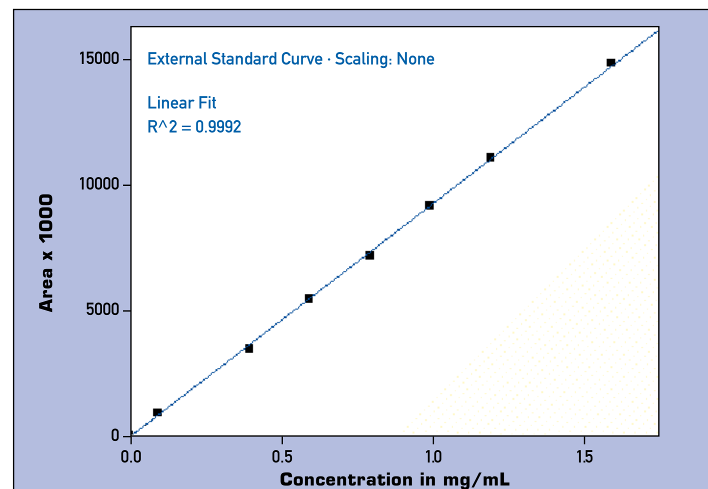


Figure 2: Calibration curve in concentration range of 0.05 up to 1.6 mg/mL. The areas are represented as in Figure 1 and calculated after background subtraction. The regression coefficient is r^2 = 0.9992

- Complete package for determination of oil in water
- Fast-GC is a suitable analysis method regarding productivity
- High sample throughput and high efficiency

In the determination of oil in water it has not been possible to date to substitute trichlorotrifluoroethane, used in the DIN norm 338 409/procedure H18 (FTIR). Therefore the working committee DIN NAW 1.3 has decided in November 1999 to withdraw the standard DIN 38 409, Part H18.

Alternatives to H18

As an alternative the procedure H53 is part of a European norm DIN EN 9377-4. This procedure uses liquid-liquid extraction of the water sample and subsequent gas chromatographic separation using a flame ionisation detector (FID). Cyclohexane, n-hexane, iso-hexane and petroleum ether are suitable extraction solvents.

Essential considerations for the analysis are:

1. No discrimination of higher-boiling components relative to low-boiling components. A non-discriminating injector, such as the OCI-2010 on-column injector, should therefore be used. The ratio of C40 to C20 signals in the chromatogram should be larger than 0.8.
2. A data acquisition system should allow the possibility of subtracting blank chromatograms (injection of pure solvent).
3. Integration is carried out from n-nonane (or n-decane) to n-tetracontane as one structure with horizontal baseline.

Complete solution for the determination of oil in water

Using the GC-2010 with on-column injector and GCsolution software in combination with the AOC-20I/S autosampler, Shimadzu offers a complete package for the determination of oil in water, which complies with all requirements of the new norm. The C40 to C20 ratio was determined after injection of an alkane mixture and was approximately 0.97, markedly higher than the required value of 0.8. So sample discrimination was ruled out. The GC system is calibrated with a mixture of two oils: a diesel oil (type A, low boiling point range), which will show well-resolved peaks in the chromatogram, and a lubricating oil (type B, higher boiling range), which contains non-resolved components.

In order to guarantee accuracy, it is important to record blank chromatograms of pure solvent for background subtraction. After subtracting the background, the area between n-nonane (n-decane) and n-tetracontane is used to calculate the signal. The calibration range should be adjusted to the expected concentration after extraction.

Figure 2 shows the calibration curve in concentration range of 0.05 up to 1.6 mg/mL extract. The regression coefficient with a value of r^2 = 0.9992 is excellent and represents a measure for the reliability of the results after background subtraction and integration. Based on this calibration, the concentrations of real samples could be determined. The waste-water sample was first filtered through a folded filter and subsequently liquid-liquid extraction with cyclohexane was carried out in a separatory funnel. The organic phase was separated and evaporated down to 8 mL. 1 µL of the extract was then injected into the GC system. Figure 3 shows the resulting chromatogram. A concentration of 1.034 mg/mL was calculated from the calibration. The hydrocarbon index ρ could be subsequently calculated in accordance with H53: ρ = 16.46 mg/L.

Fast-GC in oil analysis

In many laboratories productivity, and therefore analysis time, plays an important role. Fast-GC has proved to be a suitable method. The separation efficiency of capillary columns increases linearly with decreasing internal diameter. However separation efficiency only increases by the square root of the column length. For Fast-GC it is, therefore, best to use relatively short columns with small internal diameter and low film thickness.

For oil analysis, however, columns with very small internal diameter as well as low film thickness are not entirely suitable, since the samples are injected directly onto the column and the column capacity needs to be taken into account. As a compromise, a 15 m RTX-5 (Restek) column (0.25 mm internal diameter, 0.25 µm film thickness) with an uncoated precolumn (retention gap 2 m, ID = 0.53 mm) was used. The resulting chromatogram shows the improvement in analysis time which can be obtained when using hydrogen as carrier gas, without loss of separation efficiency. Using a GC-2010 with high-power oven allows high heating rates. The chromatogram in Figure 4 was obtained at a heating rate of 100 °C/min.

The retention time of C40 was less than 6 min. This guarantees high sample throughput and very high efficiency.

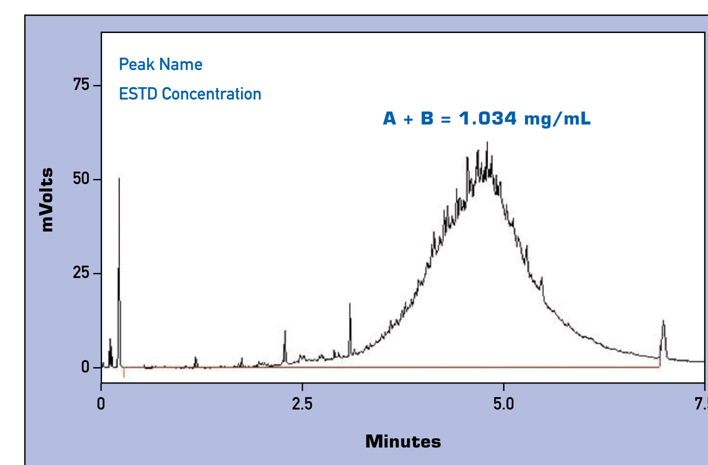


Figure 3: Chromatogram of the extract (8 mL) of a wastewater sample. The injection volume was 1 µL

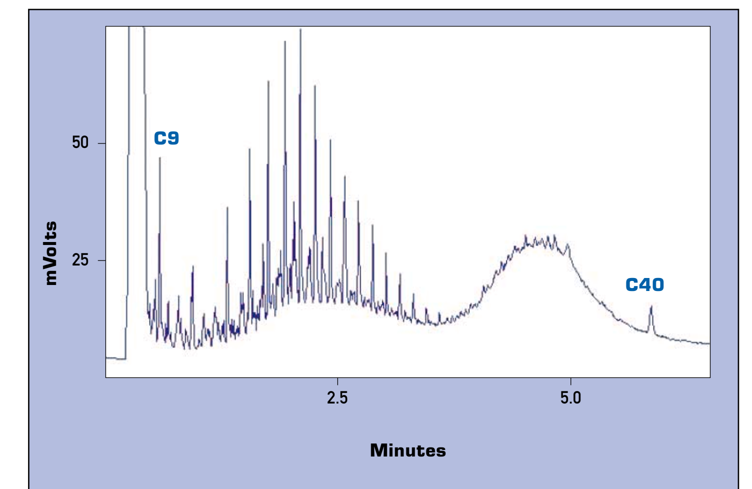


Figure 4: "Fast-GC" of an oil standard. Carrier gas: hydrogen, linear gas velocity: 143 cm/sec, Temperature program 70 °C 1 min, 100 °C/min to 320 °C 4 min

BETX in water and alde hydes determination in printed colours

Headspace Gas Chromatography with AOC-5000/GC-2010

Syring type headspace analysis with sampler is very reproducible tool

Headspace sampling technique in general is performed in two ways:

1. Syringe type sampling: The sample is transferred via a gas tight heated syringe into the injector. Incubator and syringe are heated to freely defined temperatures.

2. Transfer line headspace technique: Here the sample is transferred via a capillary into the injection unit. The latter needs a pressure gradient to the injection unit for successful transfer of sample resulting in a pressure superimposed on the column head pressure. For GCs with electronic pneumatic control this results in a split ratio which has to be corrected. Syringe type samplers do not have this problem and in addition there are no valves involved in the sampling process.

The AOC-5000 is a syringe type automatic xyz robot which has maximum flexibility in programming injection steps and sample treatment such as temperatures for syringe and incubator (orbital shaker) as well as sample injection speed. To test instrument reproducibility in this paper a solution of 5 and 100 ppm BETX in water was prepared. These types of solutions are well suited as a test for the reliability of the injection technique. For this 5 mL water spiked with the BETX standard was put into a 20 mL headspace vial. 10 samples were prepared and put into the autosampler tray. Figure 2 shows 5 successively recorded chromatograms (100 ppm) plotted above each other. Sample was taken only once per vial. The incubation treatment was 60 °C for 15 minutes and the injected volume was 1 mL into the SPL-2010 with a split ratio of 5:1. The components identification is indicated in the figure. The column used was a SE 54 50 m with 0.25 mm ID, 0.5 µm film. The p- and m-Xylol is not separated by this column. To achieve this a carbowax column 50 m, 0.5 mm has to be used. The relative standard deviation for ten runs was calculated to be below 2.5 %, which demonstrates that quantitative analysis can be carried out with headspace analysis with very high accuracy. The chromatograms were recorded with constant linear velocity mode selected on the GC-2010. This mode supplies a pressure program automatically adjusted to the temperature program so that the carrier gas velocity is kept constant over the entire analysis. This ensures a better resolution at higher temperatures according to van Deemter curves, and in addition reduces analysis time.

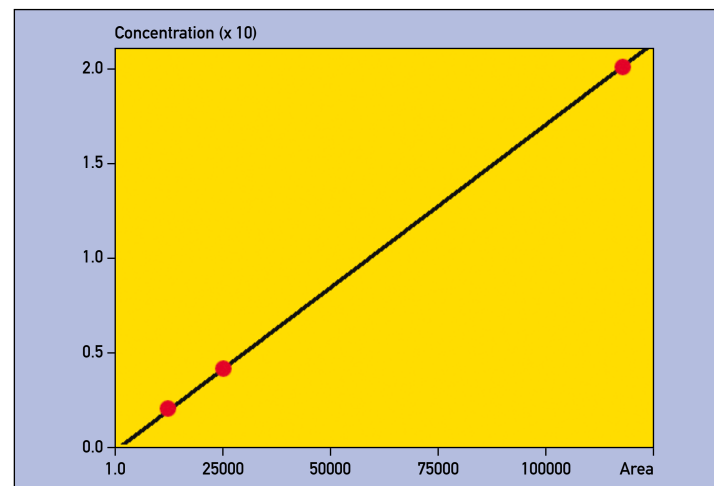


Figure 1: Calibration curve for butanal

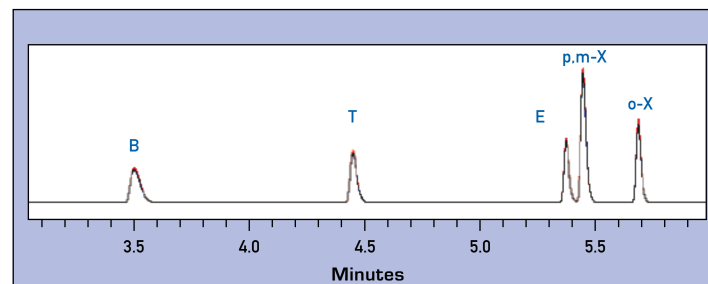


Figure 2: Five chromatograms – taken by BETX-Standards 100 ppm layerd

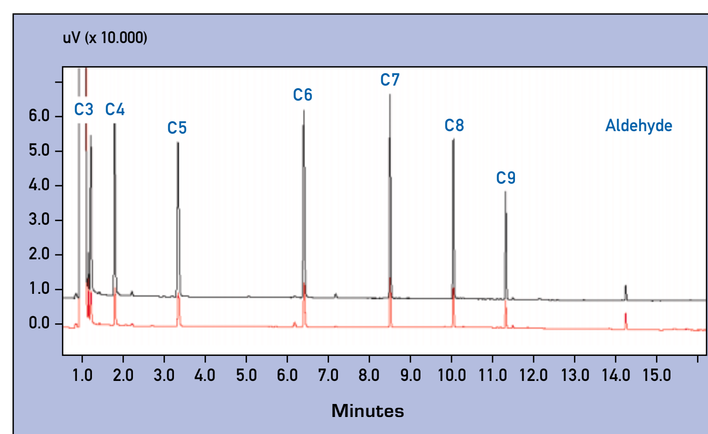


Figure 3: Chromatograms of the aldehyde standards 2 und 20 ppm

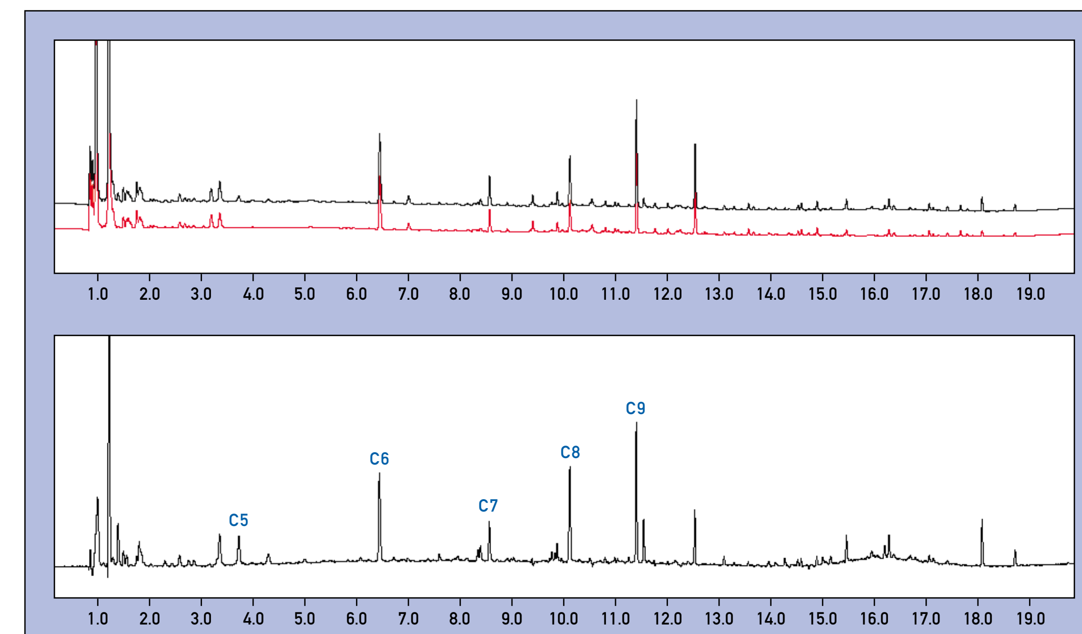


Figure 4: Top: Chromatograms from note paper with and without colour. Bottom: Differential Chromatogram

Instrumentation:

Gas Chromatograph: GC-2010AF

Column: SE54 – 50 m, 0.25 mm, 0.5 µm
RTX-5 – 30 m, 0.32 mm ID, 1 µm

Injector: SPL-2010, 150 °C (BETX),
180 °C (Aldehyde)

Detector: FID 280 °C

Software: GCsolution

Autoinjector: AOC-5000, 60 °C, Agitator for 15 min, Syringe Temp 70 °C (BETX)
100 °C, 1 h, Syringe Temp 120 °C (Aldehyde)
Injection speed 500 µL/min

Chromatographic conditions:

Carrier Gas: H_2, 40 cm/sec constant (BETX), 70 cm/sec (Aldehyde)

Split: 5:1

Col Oven: 40 °C, 1 min, 20 °C/min, 170 °C (BETX)
40 °C, 5 min, 15 °C/min, 280 °C, 10 min (Aldehyde)

After having performed a system test with BETX standard samples the system was used to determine C3-C9 aldehydes in colours printed on paper such as on journals, packages of goods etc. Here a writing pad was investigated. For calibration an aldehyde standard was prepared at 2.5 and 20 ppm solution in methanol.

100 mL of such a solution was placed into a 20 mL headspace vial. The incubation temperature was chosen to be 100 °C for 1 hour in order that both standards and samples should have the same conditions. Figure 3 shows the resulting chromatogram recorded with a RTX-5 30 m, 0.32 mm ID, 1 µm column. The linear velocity was 70 cm/sec (H_2) and kept constant (velocity mode of GC-2010). After recording the standards the calibration curves were created. As an example Figure 1 indicates the result for C4 aldehyde. The correlation coefficients are R^2 = 0.99989 which also indicates the accuracy of the setup.

After having carried out the calibration the real samples were measured. The aldehyde content of the paper is determined by the desorption of C3-C9 aldehydes from paper without any sample preparation by using the following procedure:

Sample Treatment: Two pieces of 130 cm² size were cut from the paper of interest and put into 20 mL Headspace vials. One piece had printed colour and one did not, so as to enable blind value subtraction.

Figure 4 top shows the chromatogram recorded from a writing pad with some colour printed on it. The chromatogram plotted beneath was recorded from the blank paper which already indicates some aldehyde contamination. The data shown at the bottom of Figure 4 was calculated by subtraction of the plot recorded with blank paper from the one with colour print. The result indicate a dominant C9 peak. The calculated concentrations from the calibration are:

	ppm	mg/m²
Propanal	2.69	0.2
Butanal	0.38	0.029
Pentanal	0.38	0.029
Hexanal	0.75	0.058
Heptanal	0.32	0.024
Octanal	1.15	0.089
Nonanal	2.09	0.16

Conclusion:

Syringe type headspace analysis with a highly flexible sampler such as the AOC-5000 has been proven to be a very reproducible tool for typical headspace application like BETX in water or the aldehyde determination in printed colours demonstrated in this paper.

Super fast and sensitive

Organophosphorus pesticide determination using the GCMS-QP2010

- Chromatographic methods offer very reliable tools for the qualitative and quantitative determination of pesticides in food- and environmental samples
- GCMS-QP2010 offers a maximum in sensitivity
- Fast-GC delivers results almost immediately

The analysis of organophosphorus pesticides in environmental- and food samples is one of the most challenging tasks in analytical chemistry. The numerous food scandals in recent years demonstrate the immense importance of comprehensive quality control.

Therefore it is necessary to detect the contaminants of interest at the lowest possible concentration levels in the sample. Analytical instrumental procedures, especially the chromatographic methods offer very reliable tools for the qualitative and quantitative determination of pesticides in food- and environmental samples.

Excellent detection sensitivity and unequivocal identification of hazardous compounds can be obtained using Shimadzu's GCMS-QP2010 instrument. This GCMS system offers a maximum in sensitivity. In the EI mode compounds can be unequivocally identified via their classical EI spectra, acquired in the scan mode. This is performed via comparison with a comprehensive library of mass spectra (for example NIST, Wiley). Negative chemical ionisation (NCI) is especially suitable for highly sensitive detection of organophosphorus pesticides. Using this ionisation method, it is possible to achieve quantitative and accurate determinations down to the fg-range. NCI is a selective analytical technique which enables the detection of compounds that, on the basis of their chemical structure, are able to capture electrons. NCI applications are, for example, the detection of chlorinated pesticides and phosphoric acid ester pesticides (for example lindane, chlorpyrifos).

SEI (simulated EI) and NCI can be carried out on the GCMS-QP2010 without hardware modifications with the same ion source. The user simply indicates in the GCMSsolution software which ionisation mode is to be applied for the analysis. The system is then optimised automatically via a tuning procedure.

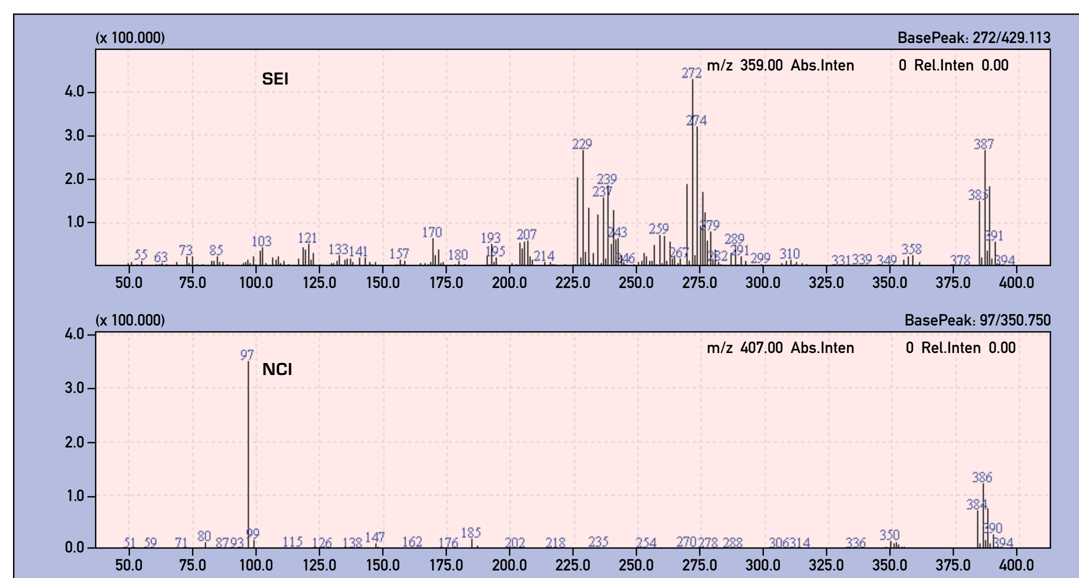
Precise Fast-GC

Time plays an important role in pesticide analysis. The analysis results must be available as soon as possible so that, in the case of positive results, the necessary measures can be taken immediately. Also in this respect, the GCMS-QP2010 lives up to its outstanding qualities: with the proven GC-2010 system in the Fast-GC mode, results become available almost immediately. Important features are the high scan rate of the MS detector of up to 10,000 amu/s and the high data acquisition rate (up to 50 spectra/s). These features allow, also for peaks with a width of significantly less than 1 second, acquisition of accurate mass spectra that are suitable for matching against an MS library.

Figure 1 shows the chromatogram of a pesticide standard using Fast-GCMS in the SEI and NCI scan mode. A 10 m column with an internal diameter of 0.1 mm and 0.4 µm film thickness (RTX-5) was used. The chromatograms were obtained in the constant linear velocity mode using a carrier gas velocity of 50 cm/s. The retention time for the pesticide endosulfan sulphate was less than 6.5 min.

Endosulfan sulphate and another pesticide, chlorpyrifos, have been detected in a tea sample. Figure 2 shows the NCI data of a mixture prepared with a non-contaminated matrix (spiked with 0.5 pg of each component) and the result of the actual tea sample (method DFG S19). Unequivocal identification of endosulfan sulphate and chlopyrofos can be obtained down to the low fg range.

The data impressively demonstrate the suitability of Fast-NCI/GCMS for the determination of organophosphorus pesticides for natural matrices at very high sensitivity and precision. This is an important prerequisite in routine analysis.



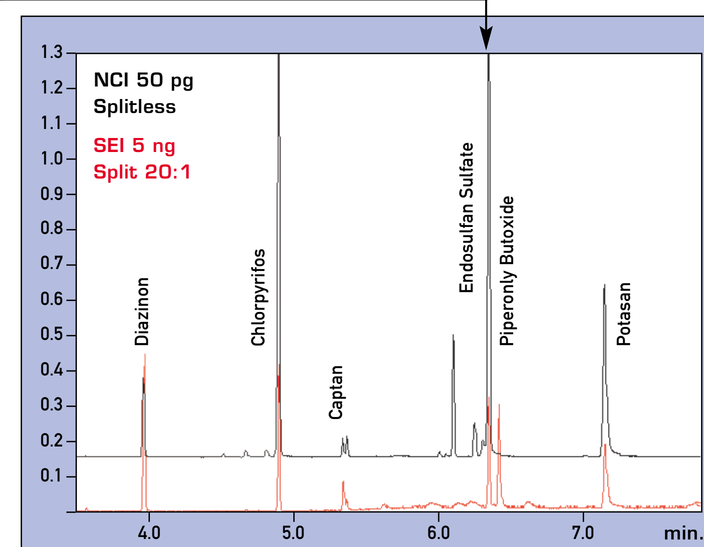


Figure 1: Fast-SEI and NCI-Scan of an organophosphorus pesticide standard

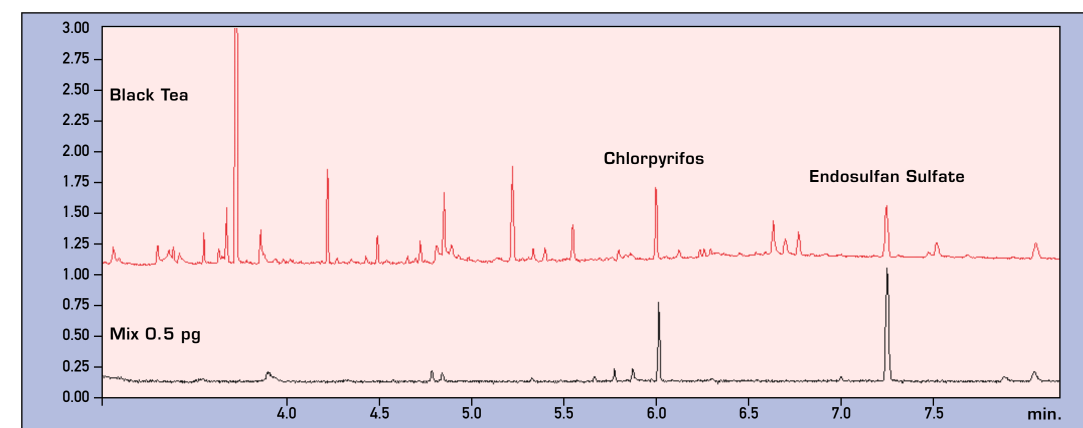
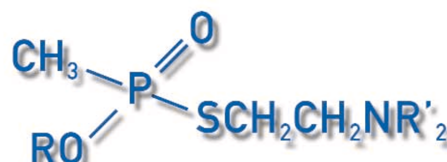


Figure 2: Fast-NCI-Scan of a standard and a real tea sample

GCMS helps to chemical disarmament

Dr. E. Savel'eva, Institute of Hygiene, Occupational Pathology and Human Ecology, St.Petersburg, Russia
Professor Dr. I. Zenkevich, Chemical Research Institute of St. Petersburg State University, St.Petersburg, Russia

The V-type chemical warfare agent VX [O-ethyl S-diisopropylaminoethyl methylphosphonothioate] and its isomer, Russian VX [O-isobutyl S-(2-diethylamino) methylphosphonothioate] are highly toxic, persistent and included among the stockpiles of the United States and the former Soviet Union. The complete formula for V-type nerve agents is:



For the most "traditional" compounds of this series known since 1950, i.e. (VX) R = Et, R' = iso-Pr and for Russian VX (RVX) R = iso-Bu, R' = Et.

The process proposed and used in Russia for destruction of phosphorus-containing warfare agents includes chemical processing by mixtures of reagents containing potassium isobutylate followed by treatment of the formed reaction mixture with bitumen. As a result, so-called bitumen-salt mixtures (BSM) are prepared.

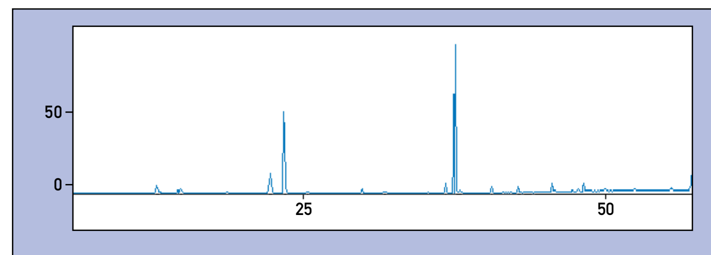


Figure 1: Typical chromatogram (total ion current) of the RVX-BSM extract by CH_2Cl_2

The goal of this work is GCMS identification of RVX decomposition products in RVX-BSM-mixtures. Up to now, only limited information on the possible formation products has been available. Accessible literature relates to VX but not RVX destruction products.

Several dozens RVX-related compounds were detected in RVX-BSM mixtures (Figure 1). The most significant feature of RVX decomposition products is low information content of their EI mass spectra (Figure 2). The typical approach in these complex cases is not to use single analytical methods, but combinations including HPLC, LCMS, GC-FTIR, GC-AED, etc. However, there is an alternative way to restrict the test methods only to GCMS, while significantly improving interpretation of GCMS data by extra processing of GC retention indices (RI).

Determination and calculation of GC retention indices

For determination of GC retention indices (RI) the retention times of *n*-alkanes C_6-C_{20} and C_{21}-C_{26} have been determined in an artificial mixture and diesel fuel of common grade, respectively. The lin-log RIs have been calculated using simplest QBasic program. To predict the structures of unknown components the RI values published in [1] for another set of compounds relevant to RVX were recalculated. Reference RI values on standard non-polar polydimethyl siloxane stationary phases for evaluation of ΔRI increments have been taken from the private collection of one of the authors (I. Zenkevich).

Instrumentation

Mass Spectrometer: QP-5000
Gas Chromatograph: GC-17A

Results

26 components were identified in RVX-BSM by means of concurrent interpretation of MS and GC data. GCMS allows both characteristics to be obtained in the same run. Thanks to high repeatability of flow and temperature control the GC-17A ensures stable retention times for the components day after day, even after column reinstallation. So daily RT control was not necessary although RT values for the components were taken from different runs. Signals in mass spectra were also highly repeatable. The content of the "most suitable" sample and RIs of the components identified in the samples are listed in the table. Seven non-volatile compounds have been found as TMS (S1-S3) and methyl (M1-M4) derivatives. The total list of sample preparation procedures is presented in [2].

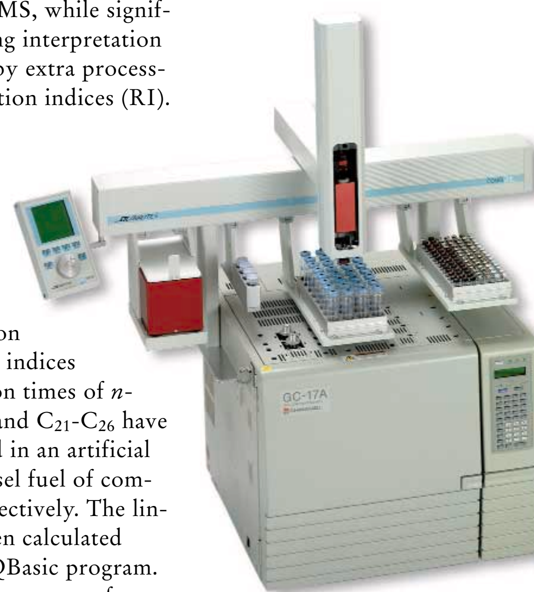


Figure 3: Modern capillary gas chromatography for routine applications with GC-17A

- Identification of Russion VX decomposition products by GCMS
- Test methods can be restricted to GCMS only due to extra processing of GC retention indices
- 26 components have been identified

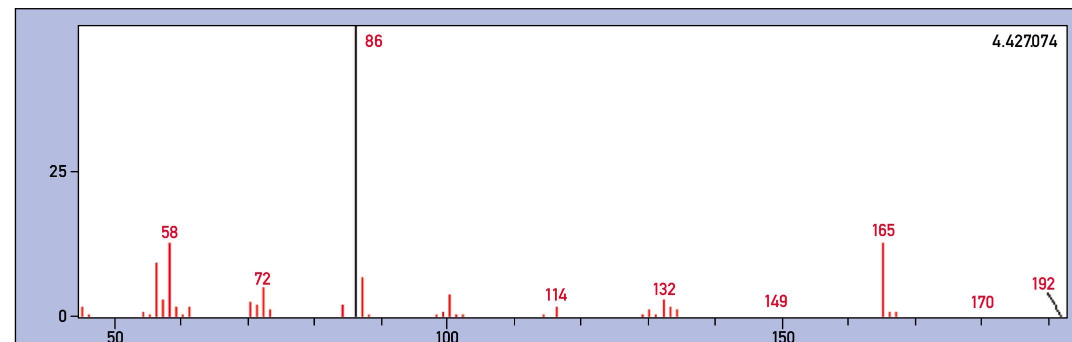


Figure 2: Mass spectrum of the principal component of RVX-BSM extract (# 18) as an example of its low information content for evaluating structure.

No.	Content %	m/z base peak	RI	RI-data for identification*	Finally proposed structure
1	2	3	4	5	6
1	11.5	58	< 700	548 ± 8 (vgl.)	Diethylamine
2	0.2	60	847 ± 1	Approximate RI evaluation	$CH_2 = CHSiBu$
3	0.9	101	930 ± 1	895 ± 2 (vgl.)	Diethyl formamide
4	2.9	86	976 ± 2	979 ± 2 (vgl.)	$Et_2NCH_2CH_2SH$
5	28.8	99	1034 ± 1	1002 ± 22 (vgl.)	N-Methylpyrrolidone**
M1	0.5	86	1076 ± 1	Formed after methylation	$Et_2NCH_2CH_2SMe$
S1	3.9	225	1142 ± 1	Formed after silylation	$MePO[OSi(Me)_3]_2$
6	0.2	86	1144 ± 2	Reduction to simpler structure	$CH_2 = CH\text{-}S\text{-}CH_2CH_2NEt_2$
S2	39.2	153	1214 ± 1	Formed after silylation	$CH_3PO(OiBu)OSi(Me)_3$
7	5.9	55	1266 ± 1	1255 ± 17 (ref.)	Caprolactam**
8	45.8	86	1292 ± 2	1297 ± 18	$Et_2NCH_2CH_2\text{-}S\text{-}iBu$
9	5.9	97	1298 ± 1	1283 ± 10	$MePO(OiBu)_2$
10	0.1	113	1331 ± 1	1336 ± 10	$MePS(OiBu)_2$
11	0.1	86	1337 ± 1	1335 ± 4	$Et_2NCH_2CH_2\text{-}S\text{-}Bu$
M2	3.2	86	1424 ± 1	1446 ± 6	$MePO(OMe)SCH_2CH_2NEt_2$
12	0.9	86	1510 ± 1	1518 ± 8	$Et_2NCH_2CH_2\text{-}S_2\text{-}iBu$
13	0.5	86	1576 ± 1	1570	$CH_2 = CH\text{-}S_3\text{-}CH_2CH_2NEt_2$
14	0.5	86	1584 ± 1	1579 ± 28	$(Et_2NCH_2CH_2)_2S$
15	0.1	86	1689 ± 1	1675 ± 8	$MePO(OiBu)\text{-}S\text{-}CH_2CH_2NEt_2$
16	0.1	86	1740 ± 1	1736 ± 8	$Et_2NCH_2CH_2\text{-}S_3\text{-}iBu$
17	2.0	86	1782 ± 1	1768 ± 8	$MePO(SiBu)SCH_2CH_2NEt_2$
18	20.8	86	1818 ± 1	1823 ± 26	$(Et_2NCH_2CH_2)_2S_2$
19	0.3	86	2010 ± 1	2030 ± 28	$(Et_2NCH_2CH_2)_2S_3$
20	0.4	86	2021 ± 1	2018 ± 3	$Et_2N(CH_2CH_2S)_2CH_2CH_2NEt_2$
21	0.6	86	2128 ± 1	2140 ± 8	$MePO(OiBu)(SCH_2CH_2)_2NEt_2$
22	5.8	86	2648	2636 ± 8	$MePO(OiBu)(SCH_2CH_2)_3NEt_2$

Table 1: A Final identification of RVX decomposition products in RVX-BSM extracts *"ref." – The identification is based on the reference RI data; all other RI values are precalculated; ** Components of reaction mixture used for RVX destruction.

Resultant data from identification of RVX decomposition products in RVX-BSM extracts is summarised in the table.

Conclusion

Detailed interpretation of GC retention indices as GCMS analytical parameters with the same importance as MS data, enables determination of reliable structures for 26 major products of Russian VX decomposition from 44 components found in RVX-BSM extracts, without the need for complex analytical methods. It is interesting to note that the ratio of identified/unidentified compounds is quite close to that of other contemporary works in this area. In spite of the application of chemical ionization mass spectra, the structures of 11 from 23 impurities in VX have been tentatively proposed [1], whilst application of modern LCMS technique identifies two thirds of 38 VX decomposition products [3].

References

[1] D'Agostino P.A., Provost L.R., Visentini J., J. Chromatogr. 402 (1987) 221
[2] Savel'eva E.I, Kusnetsova T.A., Radilov A.S and Volynets N.F. Rus. J. Appl. Chem.74 (2001) 1671.
[3] D'Agostino P. A., Hancock J.R., Provost L.R., J. Chromatogr. A. 837 (1999) 93

It's quantity that m atters

Large volume sampling using PTV injection systems in capillary gas chromatography

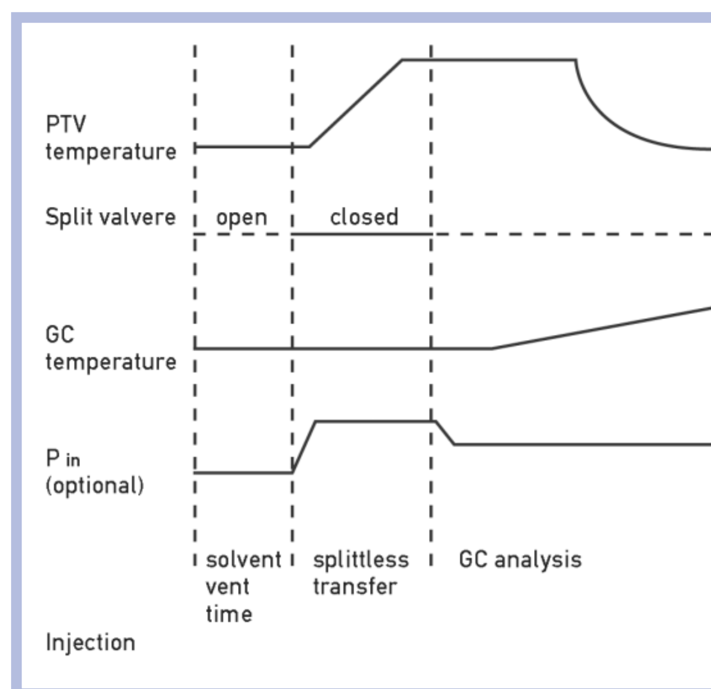


Figure 1: Worksheet for large volume injection

In recent years, large volume sampling is becoming more and more a standard technique in every laboratory. Especially in environmental laboratories where trace analysis of all kind of contaminations is a daily routine. Since the injected sample volumes are about 100 times the normal injection volumes (100 µL compared to 1 µL), the minimal detectable concentration is 100 times lower.

The advantages of large volume sampling

The conventional approach of environmental trace analysis often consists of a extraction-step of the sample with a suitable solvent, e.g the extraction of PAH's in soil or water with hexane as the extraction solvent. This can be carried out e.g. by shaking, sonication or in a Soxhlet extractor and this always results in a relatively diluted extract that has to be preconcentrated prior to injection of 1 µL into a GC instrument.

The most widely employed pre-concentration procedure is solvent-evaporation. This evaporation-method is always time-consuming and moreover, irrespective of which method of evaporation is used, there is a serious possibility that volatile components will be lost during evaporation. Besides this, when the evaporation is carried out at elevated temperatures, unstable solutes can decompose.

It will be evident from what is stated above, that important application areas of large volume injection are the improvement of detection limits in trace analysis and the reduction in the overall analysis time that can be obtained due to the elimination of the time consuming and laborious solvent evaporation step.

Large volume injection

The principle of large volume injection in GC is that the evaporation step occurs inside a liner of a PTV (Programmable Temperature Vaporizer). Temperature control and flow stability is far more better than using the pre-concentration methods mentioned above. To retain the large amount of solvent in the liner, a packing material inside the liner is required, e.g. a glasswool plug. If no packing material is used the solvent drops down to the bottom section of the liner and will, due to cold spots, evaporate very slowly. This also will lead to molecular weight-discrimination.

Temperature, flow rate and inlet pressure

Conditions during solvent venting are carefully chosen:
The temperature of the liner is just below the solvent boiling point, flow is between 200 to 250 mL/min. The inlet pressure could be decreased to obtain a more effective and faster solvent evaporation. While venting the solvent, the injector is in split mode and the solvent is eliminated via the split outlet. After the solvent is gone, the split exit is closed and the PTV temperature is increased rapidly. A standard

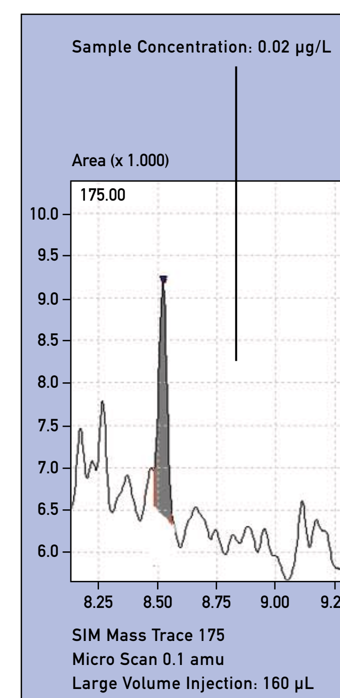


Figure 2: 100 µL injection of the pesticide Oxadiazon

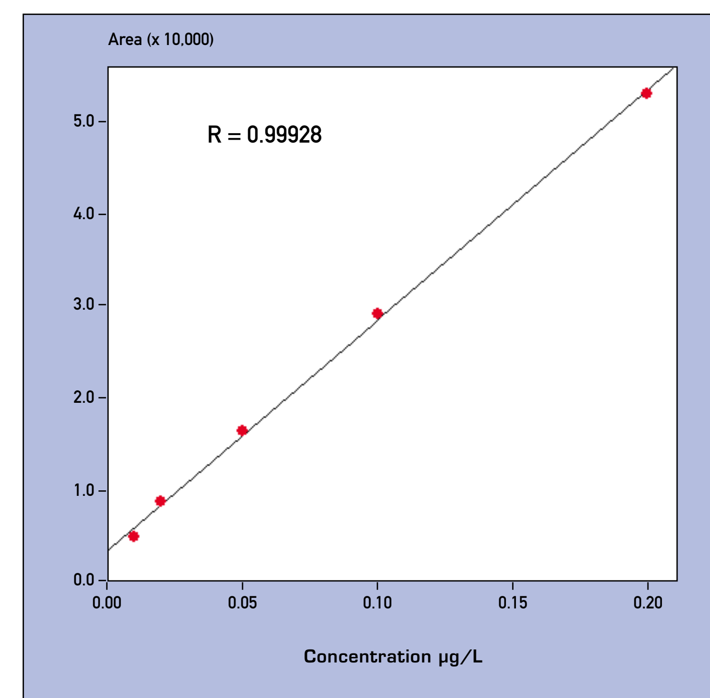


Figure 3: Calibration curve of Oxadiazon

splitless solute-transfer on to the analytical column occurs. After the solutes are transfered, the split valve opens again and the analytical separation starts. All the different steps are visible in figure 1. Some parameters require extra consideration: the choice of packing material and the inertness of the packing material.

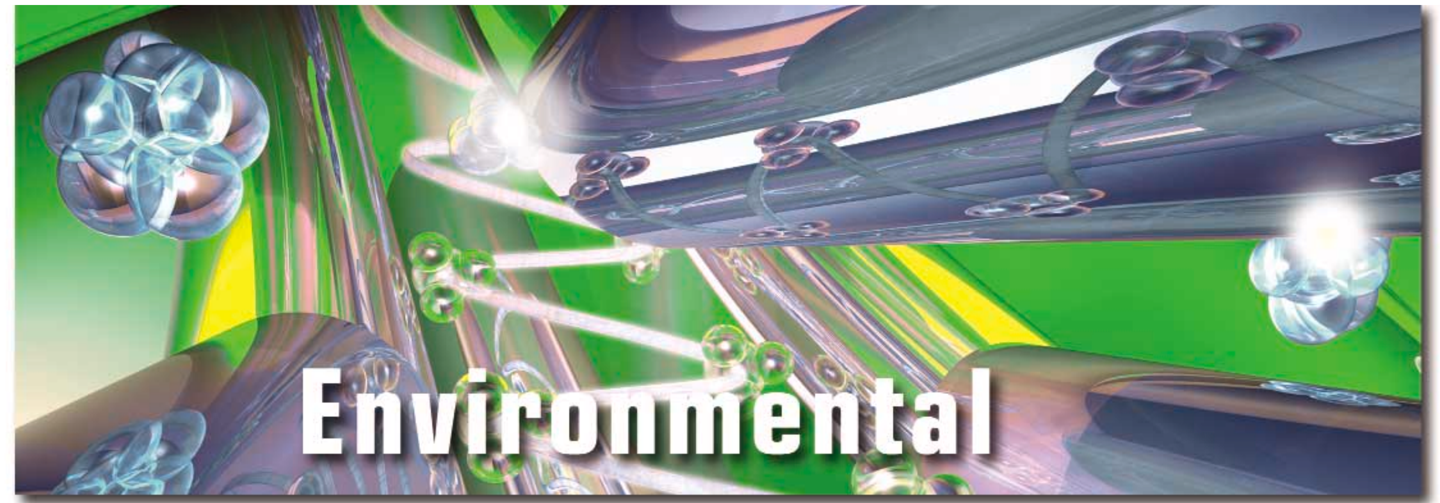
By selecting a proper packing material for the components of interest, you can gain in selectivity in your method. The packing material can adsorb some components more effective and hence obtain a better enrichment and recovery.

Volume and time are important parameters

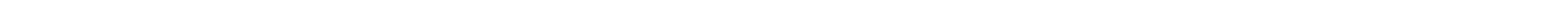
Special attention is needed for the optimization of two steps in this technique. Firstly, one has to determine the maximum solvent volume which the packed bed in the liner can accomodate. And secondly the solvent elimination time or solvent vent time, should be optimized very carefully. When the vent time is too long, losses of volatiles will be observed. Too short vent times will lead to distortion of the peak shapes, due to an excess of solvent left in the packed liner.

Figure 2 shows as an example the injection of 100 µL of the pesticide Oxadiazon in n-hexane. A detection limit down to 0.02 µg/L can be achieved with good linearity of the calibration curve (Figure 3).

- Large volume sampling becomes a standard technique
- The principle of large volume injection in GC is that the evaporation step occurs inside the liner of a PTV
- Volume and time are important parameters



Hygiene



Chromatography Volume 1
ENVIRONMENTAL HYGIENE

"Poison in textiles"

Quantitative determination of organotin compounds using the GCMS-QP2010

Analysis of organotin compounds in the eco-Umweltinstitut in Cologne, Germany (Dr. Hans-Ulrich Krieg, Managing Director)

- **TBT one of the most poisonous compounds released into the environment**
- **No legally prescribed threshold values**
- **TBT can be determined by GCMS analysis**

In January 2000, the German *plusminus* TV programme started a media frenzy with a report called 'Poison in textiles' featuring the presence of organotin compounds in, among others, soccer shirts. Although the concentration of organotin compounds found in textiles was quite low, interest in this class of compounds was awakened, particularly for the highly toxic compound tributyltin (TBT).

The *Öko-Test* ("eco test") magazine included the organotin compounds in its evaluations. A discussion began which went further than the contamination of textiles. Concerns regarding the intake through food consumption and the pollution of ecosystems by organtin compounds were raised. The internationally recognized *eco-Umweltinstitut* (Eco Environmental Institute) in Cologne, Germany, took up the challenge to react rapidly to these developments and included the determination of organotin compounds in the wide range of analyses carried out by the Institute. The range of analytical services that the Institute provides includes testing of consumer goods and furnishing materials with respect to prohibited or hazardous substances.

Use and toxicity of organotin compounds

In general, all organotin compounds are considered to be toxic. The most notorious compound is tributyltin (TBT), a very persistent and highly toxic cell poison that is difficult to degrade. TBT is one of the most poisonous compounds released into the environment, and in humans it causes damage to the hormonal, immune and central nervous systems as well as to the liver and kidneys.

The greater part of the worldwide production of organotin compounds is used as heat and ageing stabilizers in plastics, for example, PVC. These compounds are also employed as antifouling paints for ships, as pesticides, as preservatives in water-miscible and antifungal paints and as fungicides in textiles, leather, paper and wood. Synthetic fibres in particular were frequently treated with TBT, monobutyl- and dibutyltin. The organotin compounds prevent the development of an unpleasant smell in textiles during heavy sweating.

Recommended values for organotin compounds

The investigation of textiles for organotin compounds is, at present, an important part of the quality control of these products. Since there are no legally prescribed threshold values, recommended values are used for private labels and quality brands.

The *Öko-Test* magazine, for example, recommends a TBT value of 0.025 mg/kg textile, and for other organotin compounds a value of 0.25 mg/kg. The Öko-Tex Standard 100 differentiated between the categories Baby (TBT: 0.5 mg/kg; DBT: 1 mg/kg) and other categories (TBT: 1 mg/kg; DBT: not specified). The 'Association of Environment-compatible Latex Mattresses' (QUL, Qualitätsverband Umweltverträgliche Latexmatratzen) uses the following orientation values: TBT: 0.05 mg/kg and DBT: 0.25 mg/kg textile. The analytical methods described below are based on the QUL values.

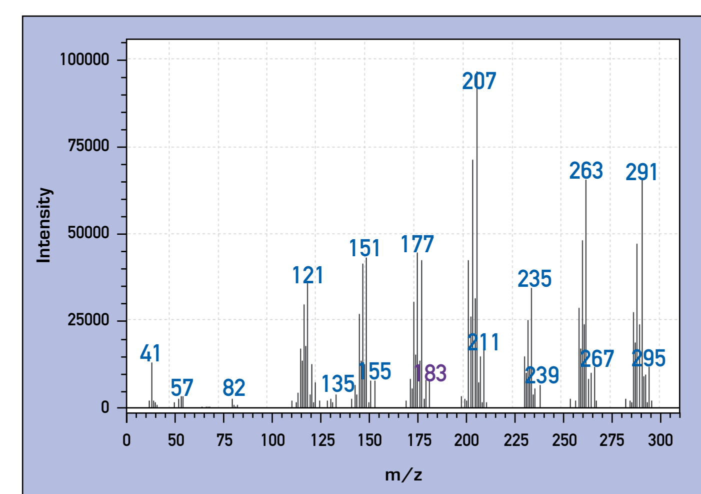


Figure 1: Mass spectrum of TBT after ethylation

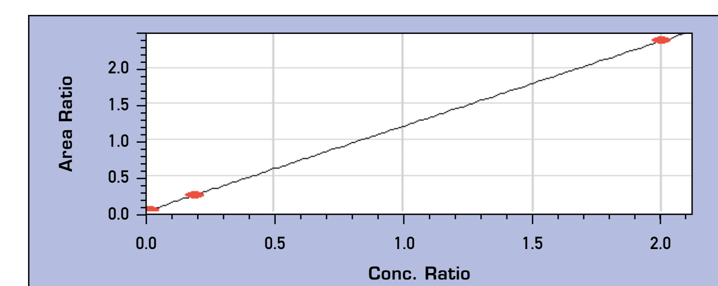


Figure 2: Calibration of TBT using the internal standard method (concentration TBT: 0.1; 1.0; 10 ng/μL)

Analysis of organotin compounds in textiles

Extraction: 2 g of the material to be investigated are boiled in acidified methanol (0.1 %) under reflux conditions for 30 minutes. During sampling, close attention should be paid to the homogeneity of the sample. If the textile consists of several different fabrics or different colours, an aliquot from each fabric or coloured part should be prepared.

Derivatization: Ethylation of the organotin compounds is performed using sodium tetraethylborate at pH 4.5 in n-hexane and takes approx. 3 - 4 hours.

Purification: After derivatization, the sample is purified over silicagel (EN DIN 38407-13D) using hexane as solvent. The final volume of the purified sample is 200 μL in n-decane.

GCMS method: The analysis is carried out using a Shimadzu GCMS-QP2010 quadrupole mass spectrometer. Separation is carried out on a capillary column DB-5, 30 m, 0.25 mm ID, 0.25 μm. Injector temperature: 260 °C, splitless injection, high-pressure injection 100 kPa, 2 min. temperature programme 60 °C for 2 min, at 8 °C/min to 160 °C, at 20 °C/min to 300 °C, holding for 2 min. Parallel to the temperature programme, a pressure programme is performed (linear velocity mode). Ion source temperature: 250 °C, interface temperature 320 °C, SIM mode.

For each degree of alkylation, organotin chlorides (for example, monoheptotin trichloride) are used as internal standards.

Summary

Tin has many naturally occurring isotopes and TBT exhibits strong fragmentation. TBT was therefore considered not to be suitable for mass spectrometric detection. TBT can, however, be determined on a QP2010 at high sensitivity in textiles using the above-described analytical method. The detection limit for the routine analysis of TBT is 0.5 ng/μL absolute – if the instrument is in good operating condition, a detection limit of 0.1 ng/μL can be obtained. In textiles, this corresponds to a concentration of 0.05 mg/kg.

This value exactly coincides with the recommended value of the QUL for TBT. The orientation values of the Öko-Tex Standard 100 are also within the range of the detection limit of this analytical method.

Tank up in the rapeseed fields

Determination of glycerine, methanol, mono-, di- and triacylglycerides

- **Shimadzu created customer specific solution**
- **GC used for analysis of fatty acids**
- **Reliable instruments and analytical experience needed**

When the German Shimadzu office in Berlin received a request for the analysis of Biodiesel in 1999 from the town of Wittenberge/ Germany, no practical information was available in this area to draw on.

Some proposed standards existed for the gas chromatographic determination of glycerine, mono- di- and triglycerides in fatty acid methyl esters (DIN 51609) and for the determination of methanol in fatty acid methyl esters (DIN 51608), the actual Biodiesel end-product. Of interest was also the gas chromatographic determination of the fatty acids as group as well as individual fatty acids and the by-product glycerine.

It is clear that gas chromatography is the important analytical method for the raw material, production control and quality assurance of Biodiesel. Today the following standards have been submitted as Euronorm-drafts:

- DIN EN 14110 'Determination of methanol content in fatty acid methyl ester (FAME)'
- DIN EN 14105 'Determination of free and total glycerine and mono-, di- and triglyceride content in FAME'
- DIN EN 14103 'Determination of ester and linoleic acid-methyl ester content in FAME'.

The biodiesel industry is a growing branch of the economy which has its roots in the 1990 Gulf crisis. Biodiesel is being developed from the viewpoint that all fossil raw materials are exhaustible.

Advantages of biodiesel

Biodiesel is considered to be an environmentally safe fuel. It is manufactured from a renewable raw material, for instance rapeseed and unlike fossil diesel is virtually sulphur-free (less than 10 ppm). Biodiesel therefore guarantees a stable and long lasting effectiveness of the oxy-catalyst. Biodiesel reduces soot emissions by 50 % because it does not contain benzene or any other aromatic compounds which form soot, and it also reduces emission of PAH (polycyclic aromatic hydrocarbons). During combustion, Biodiesel emits only the amounts of CO_2 which the plants have absorbed during growth. This significantly contributes to the fact that future EURO-III exhaust standards have already been met today.

A further advantage of the biodiesel fuel is its flash point of 170 °C, which means that it is not be classified as a dangerous substance in Germany.

If Biodiesel is released by accident, it is easily biologically degradable and does not pose any danger to the soil or groundwater. From a technical point of view, Biodiesel possesses advanced lubricating properties and will protect the engine and contains, at a highly consistent composition, up to 95 % C-18, a high ocetane number (54 - 58) and is an ideal self-igniting fuel. All in all, a real alternative to exhaustible fossil fuels and other engine technologies.

Biodiesel production

Many plant oils or animal fats are suitable for biodiesel production. Important for the selection of starting material are, for instance, the melting point (CFPP), stability (JZ), availability, raw material price and production costs. In middle European countries, rapeseed is the main raw material. First the oil is pressed from the seeds. The rapeseed oil molecule consists of the trisubstituted alcohol glycerine in which each of the 3 OH-groups is substituted by a fatty acid group. Viscosity is high at 60 cSt. Transesterification with methanol, in the presence of the catalyst sodium hydroxide, breaks the oil molecules down into glycerine and fatty acid methyl esters. The fatty acid methyl esters, more accurately the rapeseed methyl ester (RME), are extracted as biodiesel. The viscosity at this point is only 4 cSt and compares well with that of fossil diesel oil.

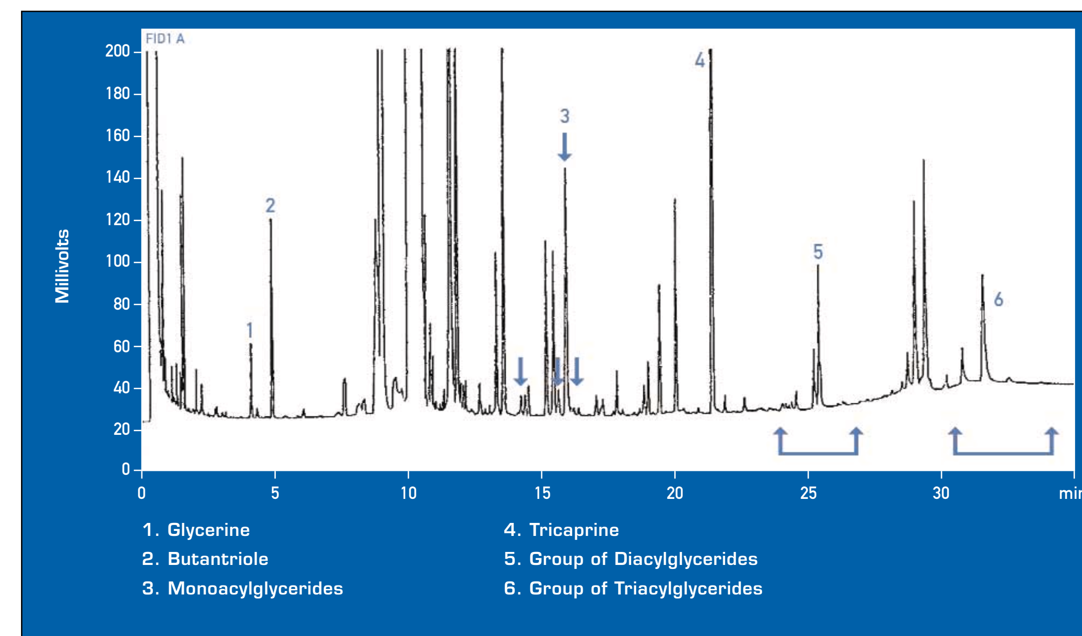


Figure 1: Example of an 'ideal' biodiesel sample. A larger representation of the three glyceride groups is shown in Figure 2

At this point it is also clear which compounds are present and what needs to be analysed. Glycerine, mono-, di- and triacylglycerides as well as methanol are determined via gas chromatography. The biodiesel end-product may contain a maximum of:

0.3 % methanol (E DIN 51608),
0.8 % mono-,
0.4 % di-,
0.4 % triacylglyceride,
0.02 % free glycerine and
0.25 % total glycerine.

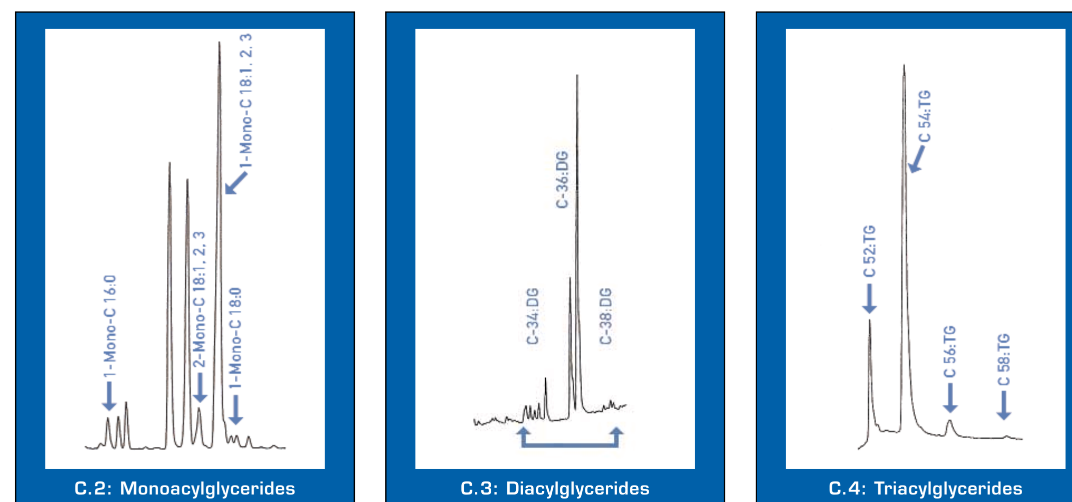


Figure 2: Enlarged representation of the glyceride groups in Figure 1

Techniques and experience needed for quality control

While the determination of methanol via headspace-GC is a routine standard method, the determination of glycerine, mono-, di- and triglycerides in fatty acid methyl esters requires reliable instrumentation and considerable analytical experience.

The DIN EN 14105 standard can be employed for FAME from rapeseed oil, sunflower oil and soya oil. The analytes glycerine as well as the mono- and diglycerides are sylilated via the addition of MSTFA in the presence of pyridine and are analysed by gas chromatography via cool on-column injection, a short thin-film high-temperature column 10 m x 0.32 mm ID x 0.1 µm film (5 % diphenylpolysiloxane) (up to 400 °C) and FID with hydrogen as carrier gas. Quantification is carried out via calibration using two internal standards, 1,2,4-butantriole for the determination of glycerine and 1,2,3-tricaproglycerine (tricaprine) for the determination of glycerides (mono-, di- and tri-).

This means that a special group-type analysis must be carried out which enables the quantification of the sum of 4 components

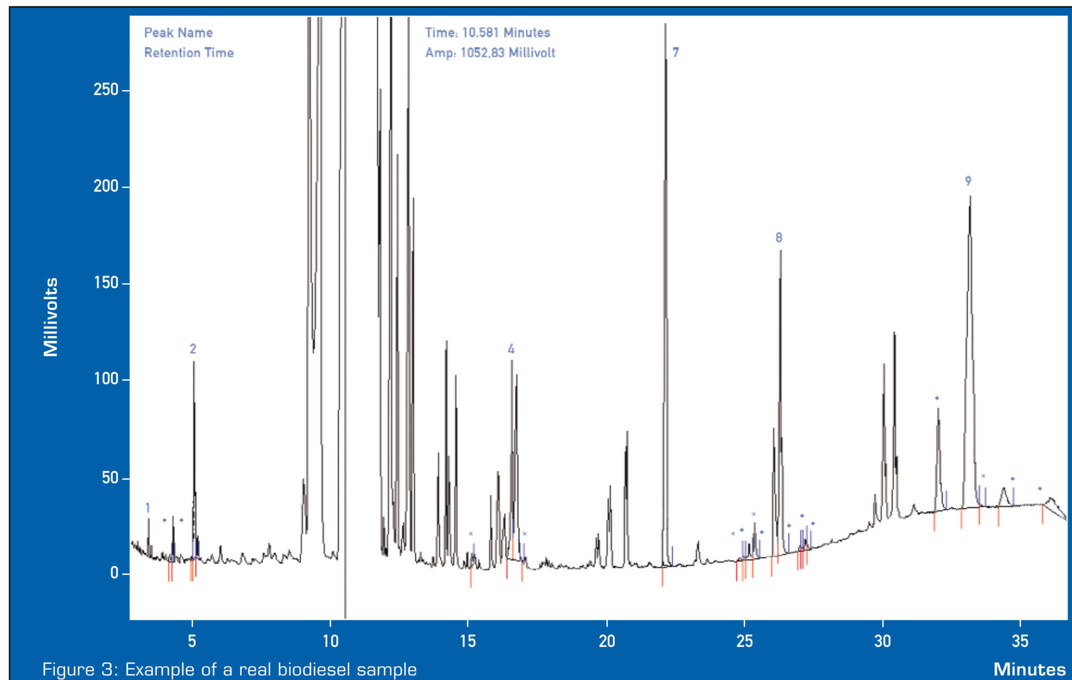


Figure 3: Example of a real biodiesel sample

Pkno	Name	Ret. Time	Conc.	Units	Area	Height
1	Glycerine	4.360	0.013	mas %	54318	24142
2	Butantriole	5.126	0.958	mas %	270038	103502
3	Mono-1	15.276	0.021	mas %	27699	7464
4	Mono-Olein	16.616	0.215	mas %	487585	107963
5	Mono-2	16.789	0.456	mas %	609343	100627
6	Mono-3	17.026	0.013	mas %	17451	4660
7	Tricaprin	22.185	0.958	mas %	1379205	280208
8	Di-Olein	26.332	0.442	mas %	784718	156884
9	Tri-Olein	33.175	1.418	mas %	2149043	155477
G2	Di-Glyceride		0.705	mas %	1312150	
G3	Tri-Glyceride		1.211	mas %	2158716	
Totals			6.410	mas %	9250266	940927
Groups	1					
1	Mono-Glyceride		0.705		1142078	

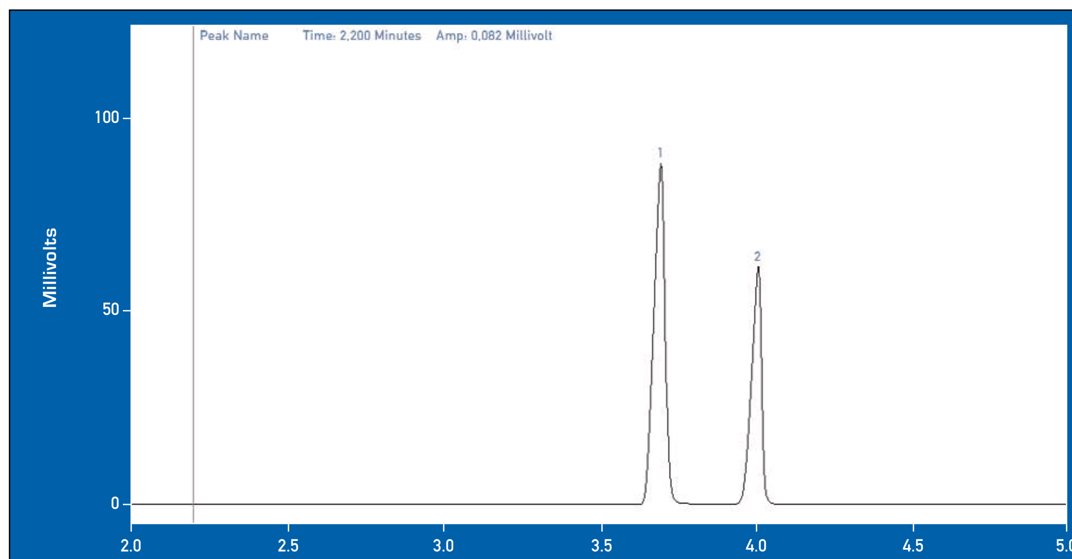


Figure 4: Example of the headspace standard: methanol with internal standard (isopropanol)

Pkno	Name	Ret. Time	Conc.	Units	Area	Height
1	MeOH	3.696	0.106	mas %	222097	88352
2	iso-Propanol	4.010	1.000	mas %	141324	61611
Totals			1.106	mas %	363421	149963

(mono) and in one time-window comprising 3 components (di and tri), using only one standard compound. The definition of a time-window for the di- and trioleins is relatively uncomplicated via the setting of start- and stop functions.

During the analysis of the monooleins, it can be seen that within the defined time-window, more than the 4 signals of interest are present. This means that the signals which do not originate from the monooleins must be excluded from the group-type analysis. This is performed preferably when the undesirable signals in the group time-window are removed from the integration via the 'Integration-OFF' function.

In the following example the main signals are indicated by numbers and stars. The experienced analyst will be able to recognise and interpret the glycerine chromatogram of the respective sample.

Shimadzu's Technical Office in Berlin has, within its sales district, up to now equipped six biodiesel plants with gas chromatographic systems and has trained laboratory personnel in the area of biodiesel analysis.

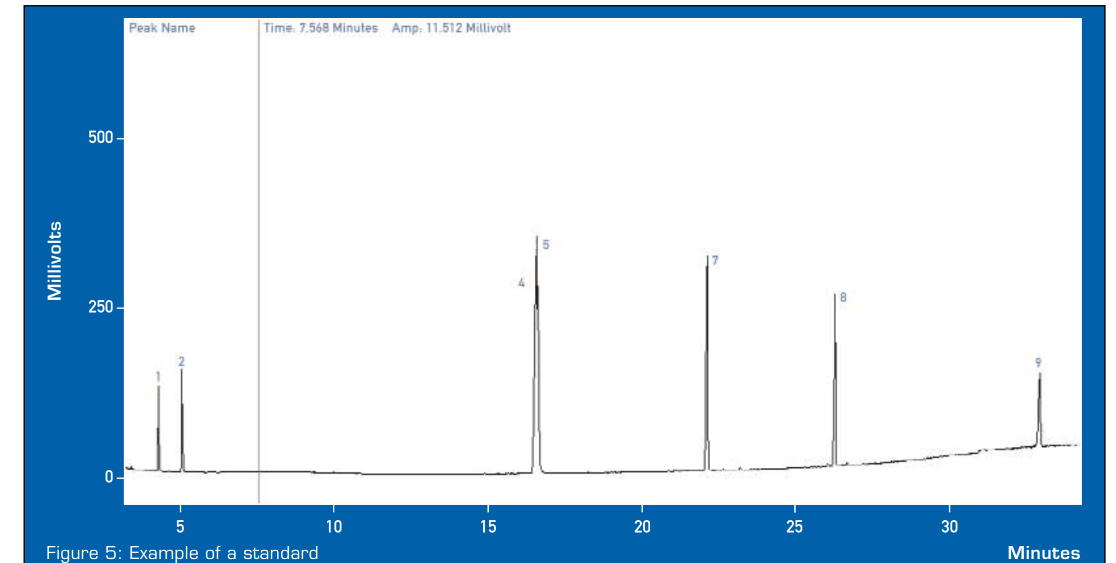


Figure 5: Example of a standard

Pkno	Name	Ret. Time	Conc.	Units	Area	Height
1	Glycerine	4.323	0.001	mas %	183136	125743
2	Butantriole	5.086	0.010	mas %	235062	150214
3	Mono-1	0.000	0.000	mas %	0	0
4	Mono-Olein	16.612	0.012	mas %	1824548	349198
5	Mono-2	16.676	0.006	mas %	767237	275435
6	Mono-3	0.000	0.000	mas %	0	0
7	Tricaprin	22.179	0.010	mas %	1282202	317261
8	Di-Olein	26.315	0.005	mas %	787290	251879
9	Tri-Olein	32.978	0.004	mas %	554149	111245
G2	Di-Glyceride		0.005	mas %	815846	650779
G3	Tri-Glyceride		0.004	mas %	7100249	1580975
Totals			0.057	mas %		
Groups	1					
1	Mono-Glyceride		0.019	mas %	2591785	

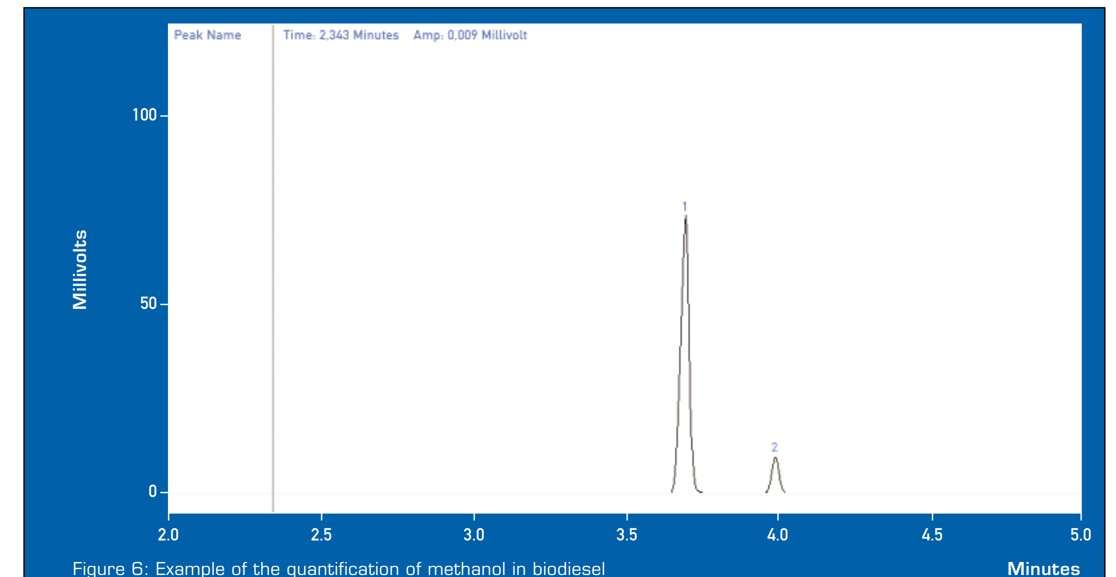


Figure 6: Example of the quantification of methanol in biodiesel

Pkno	Name	Ret. Time	Conc.	Units	Area	Height
1	MeOH	3.696	0.0159	mas %	185080	73626
2	iso-Propanol	4.010	1.000	mas %	21198	9241
Totals			1.0159	mas %	206278	82867

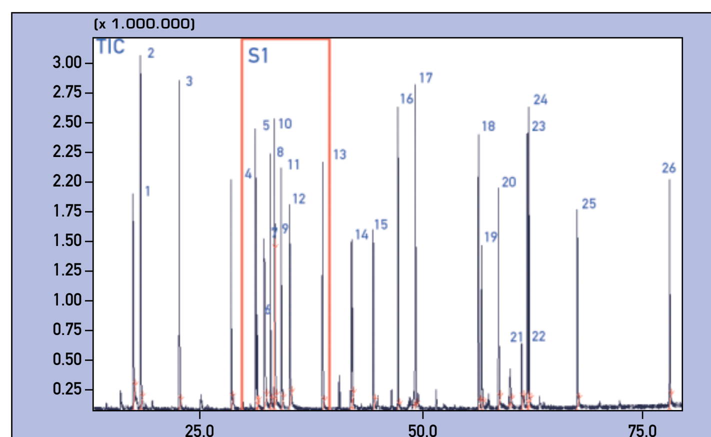


Figure 1: Total Ion Chromatogram (TIC) of an allergen standard (approx. 400 ppm, 26 compounds). Linear Velocity 34.4 cm/s (He), 50 °C 1 min, 2 °C/min up to 210 °C, 10 °C/min up to 280 °C. Split ratio 50 : 1

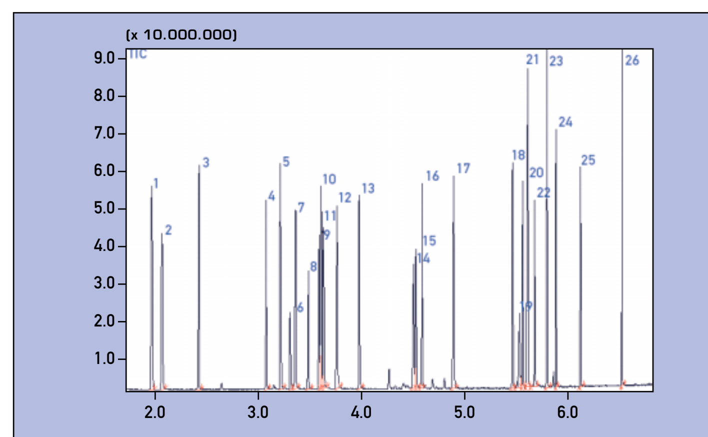


Figure 2: Allergen Mix measured with an SPB5 10 m, 0.1 mm ID, 0.1 µm Linear Velocity 40 cm/s (He), Split ratio 300 : 1, Temperature Ramp 70 °C 1 min, 25 °C/min up to 180 °C, 80 °C/min up to 280 °C 1 min. Mass range 30 - 350 amu 20 spectra/s (10.000 amu/s)

Something in the air

Fast-GCMS determination of allergens in perfumes

The analysis of allergen compounds has become more and more important as allergenic-induced diseases in human beings has increased drastically in recent years.

In particular, allergic reactions to scent of perfumes is a topic of increasing research. The problem arises from the fact that the compounds of a specific perfume can induce an allergic reaction showing differing symptoms between individual human beings. However, the analysis is very complex and time consuming. Usually this is done by using quadrupole GCMS equipment. As an example, the result of an analysis recorded with an allergen standard is plotted in figure 1.

The concentration of each compound was approximately 400 ppm with 26 compounds in total, separated on a CP SIL 5 50 m column with 0.25 mm ID and 0.25 µm film thickness. Objective is to reduce the analysis time of 75 minutes in order to enhance the efficiency of the equipment. However, analysis time cannot be reduced by changing temperature and pressure parameters using a given column without affecting the resolution.

In order to find a way of reducing analysis and cycle time while maintaining resolution, narrow bore columns have become more and more useful in increasing efficiency of analysis in different fields [1-3].

The van Deemter curves of columns with reduced inner diameter result firstly in smaller HETPmin (Height equivalent of theoretical plates) values which approach the inner diameter of the columns, and secondly have smaller slopes above the HETP minimum so that the linear velocity of the carrier gas <u> can be raised above the optimum by a factor of 2 or 3 without significant loss of resolution. This results in a drastic increase of separation efficiency as it increases in inverse proportion to the HETP value [3]. When using these columns, the instrument hardware has to fulfil some minimum requirements. These are fast sample transfer to the column, high dynamic range of carrier gas pressure and high linear temperature ramps [4].

To run the columns at optimum separation efficiency for different temperatures, the GC component should also be able to maintain mean linear velocity of the carrier gas at the different temperatures used (linear velocity mode).

In terms of detection, the system must be able to reproduce the sharp peak shapes observed in Fast-GC and GCMS [5].

The peak widths in this study are about 0.5 s. Using a quadrupole GCMS system, this means a high number of scans per second for quantitative analysis which in turn needs both a high scan speed (up to 10,000 amu/s) for the mass range scanned and a small interscan deadtime. All of these requirements are met by the Shimadzu GCMS-QP2010.

Figure 2 shows the allergen standard mix measured with an SPB5 (SGE) 10 m, 0.1 mm ID, 0.1 µm. In order to compare the resolution, segment 1 has been enlarged in figure 3.

When comparing the individual peaks, it is clear that the resolution is better with the fast analysis (citral and anisyl alcohol is resolved), with also the benefit of a speed gain of a factor of 11. For the peak widths observed (FWHM approx. 0.5 s) an acquisition rate of 20 spectra per second with a mass range of 30 to 350 amu was selected. The quality of spectra obtained with the GCMS-QP2010 is very high and yield similarity indices between 94 and 98 for the allergen compounds. Linearity was tested between 4 ppm and 400 ppm, and gave a regression coefficient of 0.99999 which also verifies the precision of the method.

The method was then applied to real samples. The TIC result of a perfume diluted in acetone (1:1000) and then injected is shown in figure 4 together with the standard (50-150 ppm). The allergens found in the dilution are Limonene (33.75 ppm), Linalool (27.77 ppm), Citral (Neral 12.3 ppm), Methyl Gamma Ionone (17.9 ppm), and Lilial (40.1 ppm), corresponding to a concentration 1000 times higher in the original material.

The data demonstrates the practical use of this fast method on real samples. Since the GCMS-QP2010 can yield up to 50 spectra per second with a scan speed of up to 10,000 amu/s, the analysis can be used as a quantitative method for allergen determination.

Description figures:

1 Limonene	8 Citral	15 Coumarin	22 Farnesol 2
2 Benzyl Alcohol	9 Cinnamic Aldehyde	16 6-Methyl-Gamma-Ionone	23 Hexyl Cinnamic Aldehyde
3 Linalool	10 Hydroxy Citronellal	17 Lilial	24 Benzyl Benzoate
4 Methyl Heptin Carbonate	11 Anisyl Alcohol	18 Amyl Cinnamic Aldehyde	25 Benzyl Salycilate
5 Citronellol	12 Cinnamyl Alcohol	19 Farnesol 1	26 Benzyl Cinnamate
6 Neral	13 Eugenol	20 Lyral	
7 Geraniol	14 Isoeugenol 1	21 Amyl Cinnamic Alcohol	

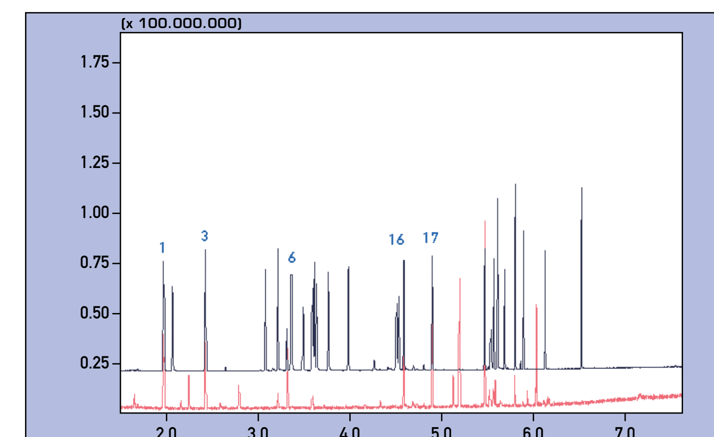


Figure 3: TICs of a perfume diluted 1000:1 in acetone and injected with the same method as figure 2. For reference, the standard is plotted above

■ GCMS as quantitative method for allergen determination

■ Narrow-bore columns increase efficiency

[1] van Es, A. High Speed Narrow Bore Capillary Gas Chromatography, Hüthig, Heidelberg, 1992
[2] David, F. et al. Abstract P53 20th International Symposium on Capillary Chromatography, Riva del Garda, Italy, May 26 - 29,1998
[3] L. Mondello, J. Microc. Sep. 12(1) 41 - 47, 2000
[4] H.-U. Baier and L. Mondello, Schnellmethoden zur Beurteilung von Lebensmitteln, Kap. 12, Die schnelle Gaschromatographie in der Lebensmittelanalytik, Behrs Germany, accepted for publication
[5] J. V. Hinshaw, LCGC (2002) vol 15 p. 152

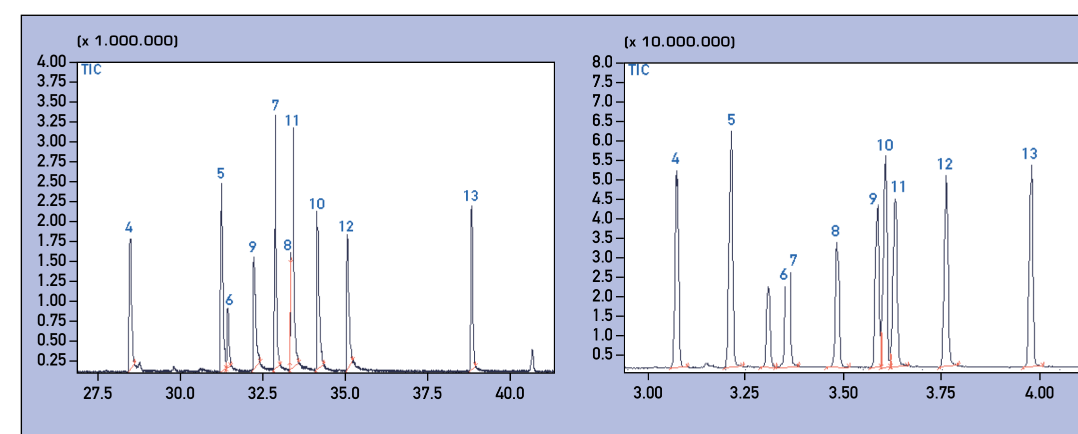


Figure 4: Peaks in the retention time segment 1 for comparison of resolution. Peak numbers are given in elutition sequence

Food Analysis

Development of a fully automated GC-GC system

The analysis of real complex samples: Essential Oils

■ Overview on multi-dimensional gas chromatography

Luigi Mondello, Maurizio Catalfamo, and Giovanni Dugo, Dipartimento Farmaco-Chimico, Facoltá di Farmacia, Universitá degli Studi di Messina, Italy

Paola Dugo, Dipartimento di Chimica Organica e Biologica, Facoltá di Scienze, Universitá degli Studi di Messina, Italy

Multi-Dimensional Gas Chromatography (MDGC) has been used for many years in many different ways. According to Bertsch, the techniques which combine two separately controlled gas chromatographic separation systems can be defined as "two-dimensional gas chromatographic techniques".

From this point of view, a multidimensional system, depending on its complexity, may be used in a combination of operational modes such as the following: Solvent-flush, Back-flush, Heart-cut.

A review of the literature indicates that GC-GC heart-cutting has been used since the mid-1950s in process chromatography either with packed-packed columns or packed-capillary columns or capillary-capillary columns.

In the early years, multidimensional GC systems regularly employed a rotary switching valve.

In 1968, Deans reported a valveless switching system which allowed no valve or moving parts to be in either the sample flow path or the higher temperature zone. This technique is based on a pressure balance between the two columns. This is made possible by inline restrictors and the use of additional makeup gas. An improvement of this system was presented by Schomburg, who replaced the original valveless column connection of Deans' system with a "live" switching system containing a special coupling unit. The two capillary columns are inserted over a thin platinum capillary which is the central component of the coupling piece. Supplementary carrier gas is added through two control lines and adjusted with needle valves.

Ten years after the introduction of the switching technique proposed by Deans, commercial instruments based on Dean's principle, enabling solvent-cutting, heart-cutting and back-flush, were developed. Systems working with mechanical valves which had been proposed earlier were not considered reliable, since the valves available at that time did not have adequate thermal stability and memory effects were likely to occur.

Technological progress of valve design rendered miniaturized connectors for the assembly of multidimensional GC systems, eliminating dead volumes. These mechanical valves are stable at high temperature and can be used to set up multidimensional GC systems without any drawbacks. They are easier to operate than those based on Dean's principle.

In the full paper, a multidimensional developmental GC system, using mechanical valves, is described for multitransfer purposes based on a high temperature valve to heart-cut fractions from the first capillary column to a second capillary column with a hot transfer line and a system to maintain a constant flow during the transfer.

The use of this multidimensional system to solve analytical problems regarding mainly the chemistry of the essential oils is also outlined.

The described configuration is a specific adaption of Shimadzu GC-17A systems done by Prof. Luigi Mondello.

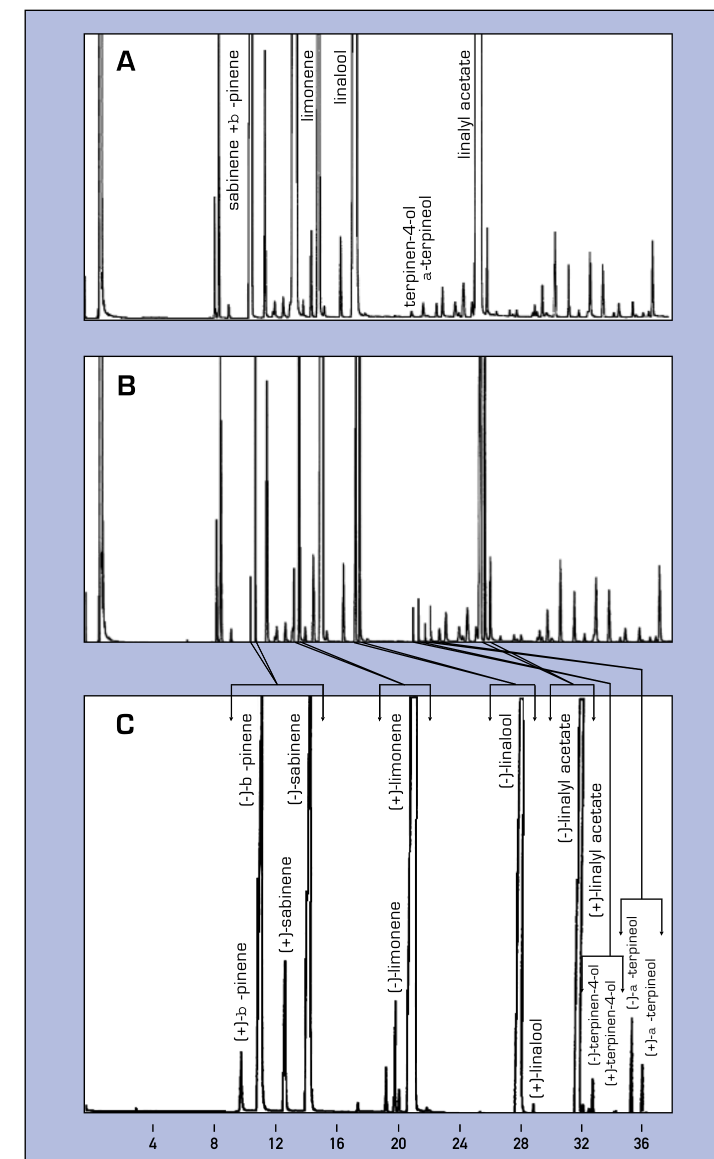


Figure 1: Analysis of essentail oil composition

16 times faster with the GC-2010

Determination of Fatty Acid Methyl Esters (FAMES) in fats and oils of animal and vegetable origins by conventional and Fast-GC analysis with the GC-2010

- Quality control in food analysis
- Analysis time is key to productivity
- Fast-GC reduces drastically retention times

Prof. Dr. Luigi Mondello in front of the gas chromatograph GC-2010

The analysis of food products is one of the important tasks in analytical chemistry. In quality control the amount of samples to be analysed per day can be quite high. Thus analysis time is an important factor for the productivity of a control laboratory. A solution for the achievement of high productivity is the application of the Fast-GC method. In Fast-GC the retention times can be reduced drastically compared to "conventional" GC methods.

For Fast-GC short columns with small inner diameters and thin stationary phase films are used. With these kind of columns retention times can be reduced without loss of resolution.

The very small inner diameter used means that you need high pressures applied to have a high linear velocity required for a good separation. This linear velocity is kept constant (constant linear velocity mode) to ensure optimal resolution for every part of the chromatogram and further reduce the retention time by reducing the elution temperature.

Very important is also the use of high heating rates for the reduction in retention time. With the GC-2010 you can use pressures up to 970 kPa and heating rates up to 140 °C/min. Of course the cooling speed is also high with 3 min from 300 °C to 50 °C.

To achieve good and reproducible data the detector sampling frequency must match the speed of the chromatography. Thus the detectors in the GC-2010 have a sampling rate of 250 Hz (4 ms interval) and a filter time constant of 4 ms (minimum). The following application was developed at the University of Messina by Professor Luigi Mondello and Professor Giovanni Dugo. It shows the use of the Fast-GC method for the analysis of Butter FAMES. It is shown that the analysis time can be reduced from more than half an hour to 2 min, i.e. a factor of 16.5!

Figure 1 shows the chromatogram for the "conventional" GC. The column used was a standard column 20 m, 0.25 mm I.D., 0.25 µm film thickness.

Linear velocity was constant at 36.2 cm/sec. Heating rate was 3 °C/min. Retention time is 33 min.

Fast-GC Analysis

Figure 2 shows the same sample with Fast-GC using a 10 m column, with 0.1 mm I.D. and a film thickness of 0.1 µm.

Linear velocity was constant at 116 cm/sec and heating rate 90 °C/min. Retention time obtained was 2 min.

The method of Fast-GC is not restricted to any type of compounds but it can be used for every kind of sample with high advantage in terms of productivity, without loss of sensitivity, reproducibility (< 1 %) or separation. We will certainly see an increased number of applications for Fast-GC in the future.

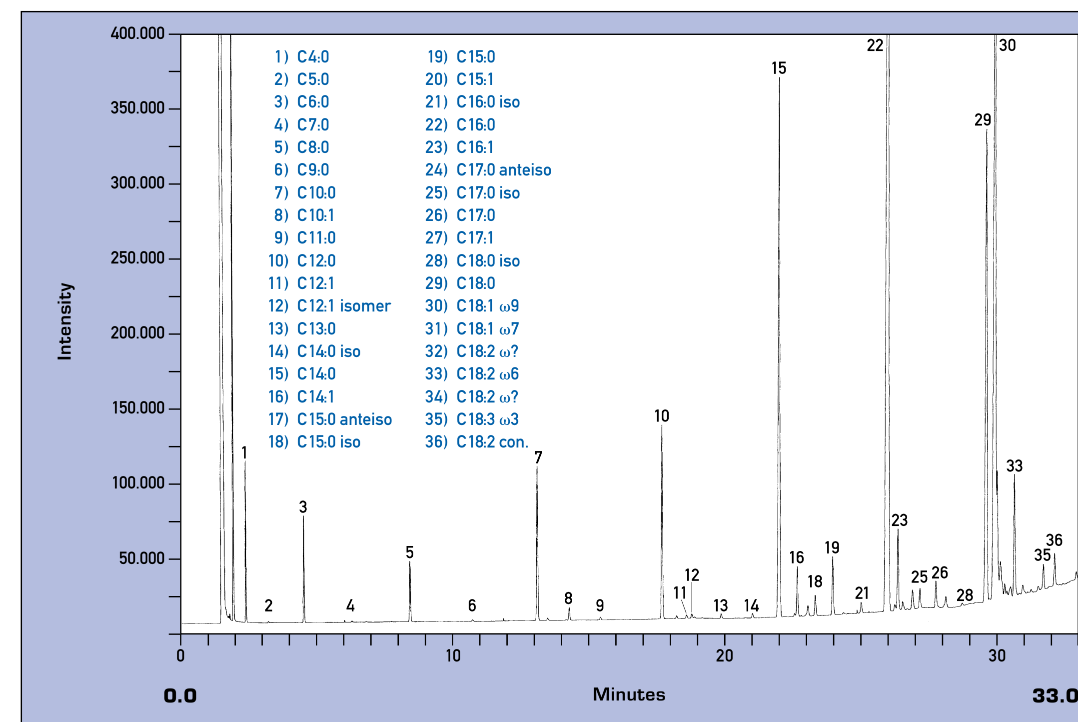


Figure 1: Butter FAMEs "Conventional" Analysis

Column: Rtx Wax 30 m x 0.25 mm i.d.
0.25 µm film Inj. Vol.: 1 µL (1:10 in hexane)
Split Ratio: 1:50 (250 °C)
T. Progr.: 50 °C to 250 °C at 3.0 °C/min
Carrier gas: H_2 Linear velocity u: 36.2 cm/sec (constant)
Detector: FID (250 °C) H_2: 50 mL/min,
Air: 400 mL/min, Make-up: 50 mL/min kPa (N_2)
Interval: 40 msec
Filter Time Constant: 200 msec

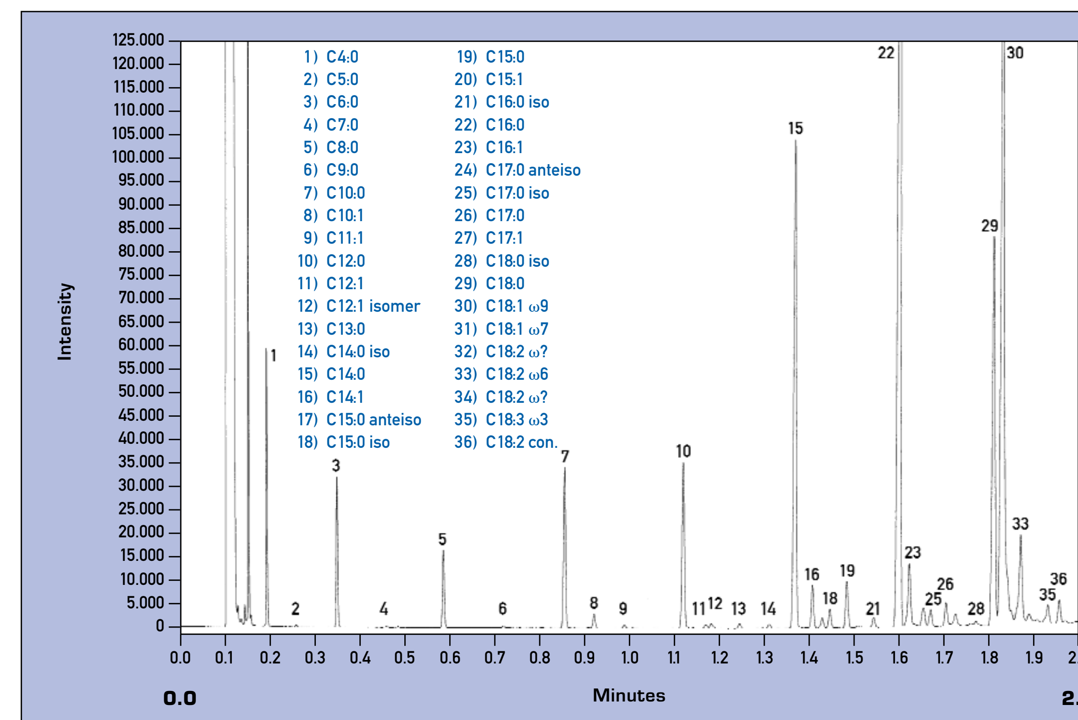


Figure 2: Butter FAMEs Fast-GC Analysis

Column: Rtx Wax 10 m x 0.10 mm i.d.
0.10 µm film Inj. Vol.: 0.2 µL (1:20 in hexane)
Split Ratio: 1:200 (250° C)
Gas save mode: after 2 min reduction of split ratio to 1:10
T. Progr.: 50° C to 250° C at 90.0° C/min
Carrier gas: H_2 Linear velocity u: 116.0 cm/sec (constant)
Detector: FID (250° C) H_2: 50 mL/min,
Air: 400 mL/min, Make-up: 50 mL/min kPa (N_2)
Interval: 4 msec; Filter Time Constant: 50 msec

Fast-GC-ECD analy sis of organo-chlorine pesticides

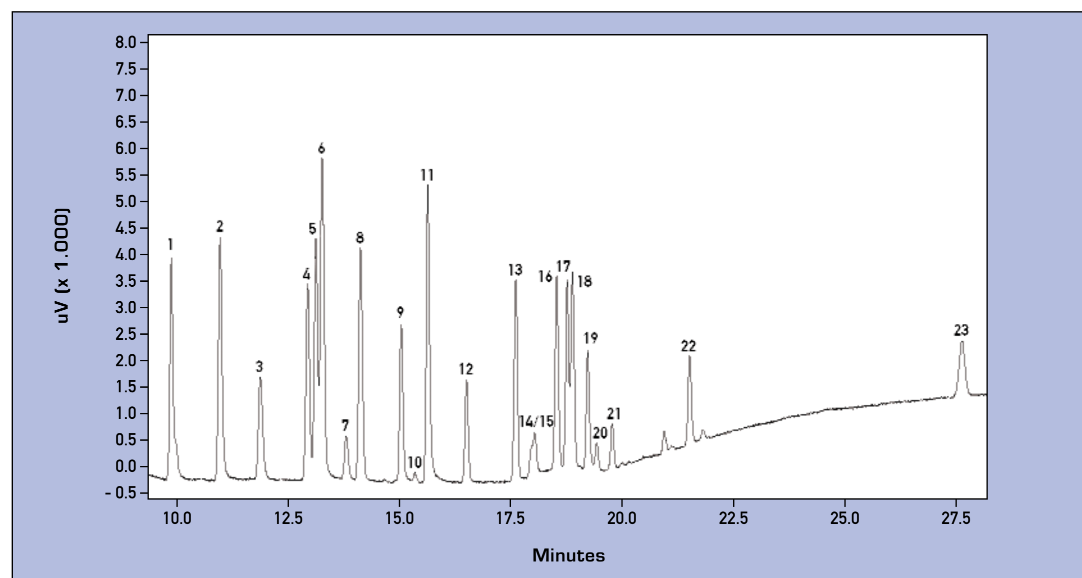


Figure 1: Standard analysis of an OCP standard (23 compounds) using an RTX-5 30 m, 0.25 mm ID, 0.25 µm film

- **Narrow bore columns have become significant in routine work**
- **Good separation, short retention time**

The analysis of organo-phosphorous (OPP) and organochlorine (OCP) pesticides in environmental and food matrices is of major importance in routine analysis. The large number of compounds to be detected requires a proper screening method in order to complete the analysis in a reasonable time.

In the search for a method which reduces analysis time while maintaining resolution, the use of narrow bore columns has become significant in routine work [1].

Although many publications exist describing Fast-GC using FID, FTD and FPD, this paper describes the use of ECD. As the peak width at half hight (FWHM) in a chromatogram recorded with 0.1 mm ID column are expected to be about 0.5 s [2], the detector needs to have low dead volume, selectable filter time constant, and to supply enough data points across the peak [3]. The latter is referred to as the sampling frequency.

With the GC-2010, it is possible to freely select the filter time constant and the sampling frequency (min. 4 ms and max. 250 Hz respectively) for all detectors.

In GC analysis using standard columns of about 30 m length with inner diameter 0.25 mm and 0.25 µm film, the typical run time for an OCP standard containing 23 compounds is about 29 minutes. Figure 1 shows the chromatogram of such a standard (for concentration refer to table 1).

The retention time of the p,p-DDD is about 21 minutes. The column used was a 5 % phenyl with a temperature program of 100 °C, 1 min, 50 °C/min to 170 °C, 1 min, then 5 °C/min to 220 °C, then 10 °C/min to 260 °C, then 20 °C/min to 280 °C, 10 min with N_2 and a starting pressure of 77 kPa corresponding to a linear velocity of 23 cm/s. The injection was carried out in splitless mode (1 µL).

This method was then transferred to the Fast-GC method using a CPsil 8 9 m, 0.1 mm, 0.1 µm and H_2 as carrier gas. The result is shown in figure 2. All 23 compounds were better separated and the retention time of p,p-DDD was less than 3.6 minutes. The program used was 80 °C, 1 min, then 60 °C/min up to 280 °C, 3 min with a initial

head pressure of 324 kPa and a mean linear velocity of 100 cm/s constant over the entire chromatogram. The filter time constant and the sampling frequency was selected as 20 ms and 63 Hz respectively.

Injection volume was 1 µL with a split ratio of 40 : 1. The signal to noise ratio of a HCH, for example is about 440 : 1 in this analysis, compared to 220 : 1 in the splitless standard measurement, indicating the increased sensitivity due to the sharper peaks. ➧

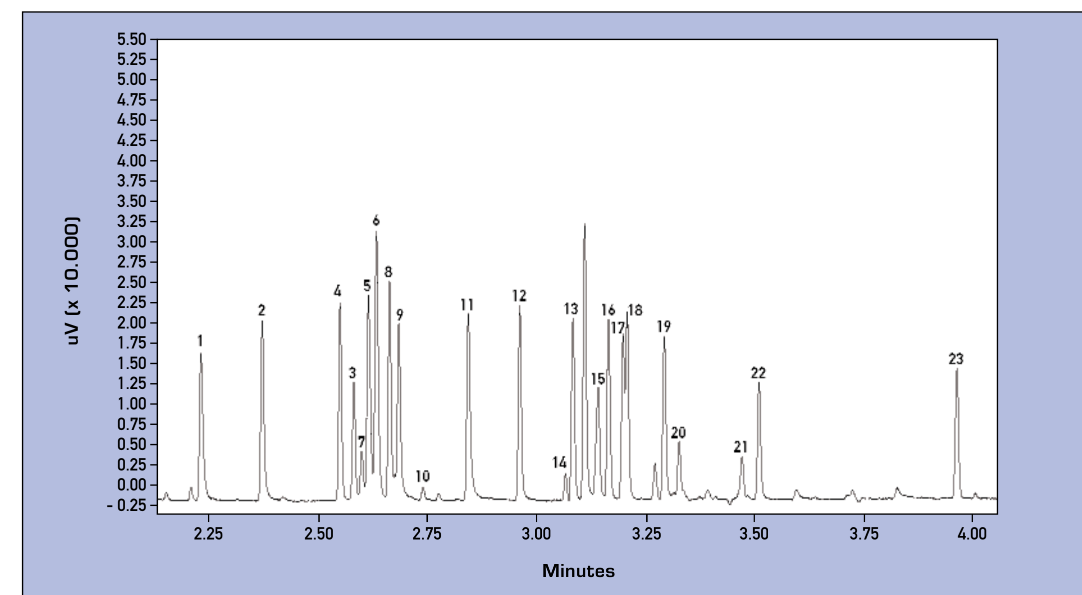


Figure 2: Fast analysis of the OCP standard containing 23 compounds (Injection 1 µL, split 40 : 1, temperature program: 80 °C, 1 min, 60 °C/min to 280 °C, 3 min. H_2 linear velocity 100 cm/s, ECD: make up gas: 80 mL/min, acquisition 16 ms, filter time constant 20 ms.

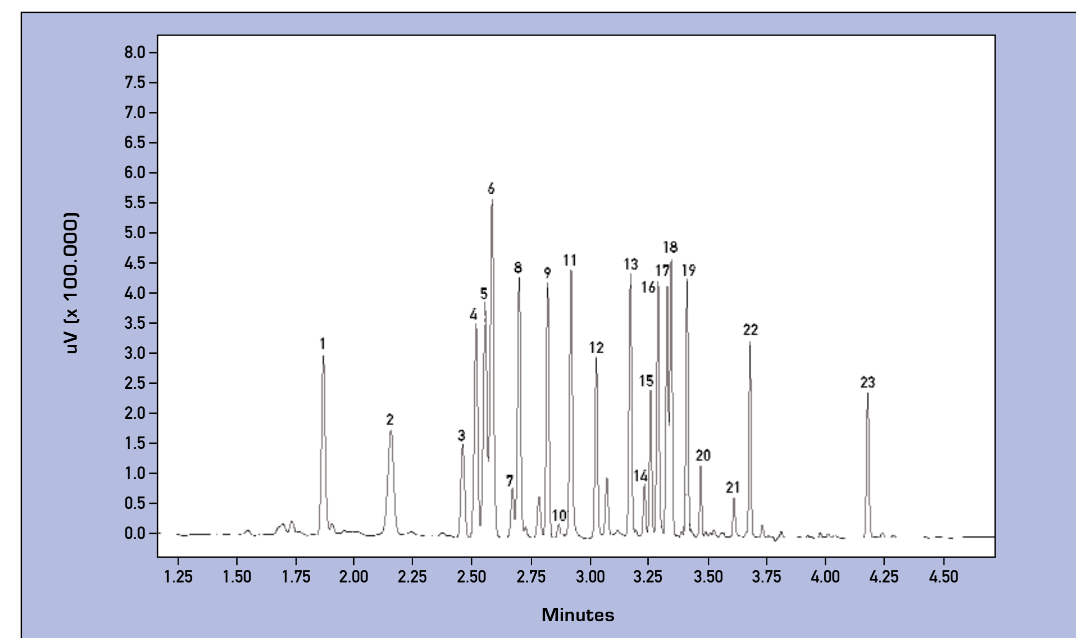


Figure 3: Chromatogram recorded with the OCP standard mix. Injection 1 µL splitless, high pressure pulse 400 kPa. Column RTX-5 10 m, 0.18 mm, 0.4 µm. Temperature program: 100 °C, 1 min, 60 °C/min to 280 °C, 3 min. H_2 120 cm/s.

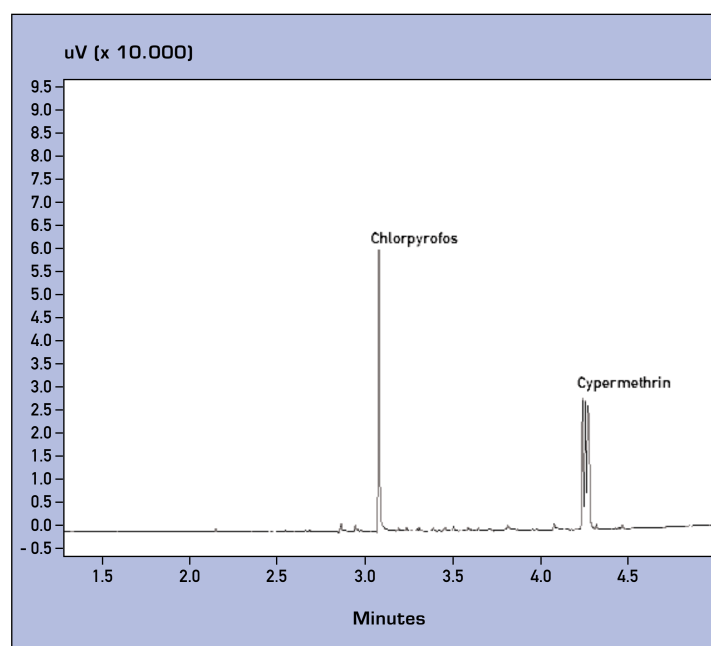


Figure 4: GPC eluate (e2 S 19) of a grape sample measured with Fast-GC-ECD: Chlorpyrofos 0.53 ng/mL (corresponds to 0.48 mg/kg grapes) and cypermethrin 0.55 ng/mL (corresponds to 0.5 mg/kg).

		RT	Conc (ppb)
01 Pentachlorbenzol	Target	2.23	21.3
02 Tecnazen	Target	2.37	22.5
03 Benfluralin	Target	2.58	52.8
04 Alpha-HCH	Target	2.548	22.1
05 HCB	Target	2.613	24.1
06 Pentachloranisol	Target	2.631	20.6
07 Beta-HCH	Target	2.598	20.4
08 Lindan	Target	2.662	28.8
09 Delta-HCH	Target	2.818	23.2
10 Epsilon-HCH	Target	2.683	1
11 Pentachloranilin	Target	2.842	26
12 Heptachlor	Target	2.96	30.4
13 Aldrine	Target	3.109	21.7
14 Isobenzan	Target	3.065	5
15 Bromophosmethyl	Target	3.139	22.6
16 Isodrin	Target	3.163	22.04
17 Cis-Heptachlorepoxid	Target	3.196	25
18 Trans-Heptachlorepoxid	Target	3.206	25
19 Bromophosethyl	Target	3.291	50.36
20 Trans-Chlordan	Target	3.325	5
21 Cis-Chlordan	Target	3.469	5
22 p,p-DDD	Target	3.508	22.4
23 Mirex	Target	3.961	21.84

Table 1: Concentration of the OCP standard

The full width at half maximum of a HCH as an example is about 0.5 s which is the typical FWHM observed with these kind of columns proving the suitability of the ECD-2010 for fast analysis in the field of organochlorine pesticides beyond doubt.

The limit of detection for a HCH, for example, is about 0.1 ppb with a split ratio of 40 : 1, requiring that the signal to noise level be at least 3 : 1.

To apply a splitless injection technique, a high pressure injection in combination with slightly thicker film on the column has to be used. This is demonstrated in figure 3.

Here a 10 m, 0.18 mm, 0.4 µm (5 % Phenyl) was used with 100 °C initial temperature and 120 cm/s. All other parameters were unchanged. Looking again at aHCH, the detection limit calculated from the signal to noise ratio is about 0.01 ppb in this case.

The analysis of pesticides is regulated by the well known multi residue method refered to as S19 in Germany and DIN EN 1528-3, DIN EN 12393-2 in Europe. The method described above was also adapted to measurement of real samples prepared according to this procedure. Figure 4 shows a chromatogram recorded with a grape eluate containing chlorpyrofos and cypermethrin. This was measured using the thin film column (see figure 2).

The determination of organophosphorous and organochlorinated pesticides in food matrices can be performed well using Fast-GC-FPD, GC-FPD and GC-ECD. With the chorinated compounds the detection limit of this method is below 0.1 ppb for several compounds using a split of 40 : 1 and about 0.01 ppb using the splitless technique with a column of increased film thickness in combination with high pressure injection.

Literature:

[1] Van Es, A.: High Speed Narrow Bore Capillary Gas Chromatography, Hüthig, Heidelberg 1992

[2] Baier, H.-U. and Mondello L.: Die schnelle Gaschromatographie in der Lebensmittelanalytik in Schnellmethoden zur Beurteilung von Lebensmitteln und deren Rohstoffen Kap. 3.2, Behrs Verlag 2004. Im Druck.

[3] Hinshaw. J.: LCGC (2002) vol 15 p. 152

Fruits, not only sweet

Comparative analysis of aroma compounds of African pears via differently coated solid-phase micro-extraction fibres (SPME) using GC-FID and GCMS

The so-called African Pear (*Dacryodes edulis Burseraceae*) is a well known plant in West Africa, with edible fruits and bark, leaves, stem and roots which have use in local medicine against various diseases. The fruit is usually eaten raw or boiled, and the pulp is also roasted to form a type of butter. Essential oil compositions are known for parts of African pear plants growing in (Democratic Republic of) Congo and Nigeria. No information however is available on the composition of the aroma compounds of the fruits.

Following a series of recent publications on applications of headspace solid phase micro extraction (HS-SPME) coupled with gas chromatography-spectroscopy (GC-FID and GCMS) for extraction and identification of aroma compounds of various fruits, flowers and spices (Bonino et al., 2003; Diaz-Maroto et al., 2002; Jelen et al., 2000; Jirovetz et al., 2001; Vercammen et al., 2000), HS-SPME is of increasing importance in the aroma analysis of exotic fruits (Jirovetz et al., 2003; Shang et al., 2002). For this reason, the combined HS-SPME with GC-FID and GCMS (GC-14 and GCMS system QP-5000 from Shimadzu, both with 2 columns of different polarity) was used for the first time in the pulp aroma compound analysis of African pear fruits from Cameroon.

A decisive point of this study was the fact that a range of different SPME fibers are already commercially available. It is also known that by using different types of SPME fibers, a dramatic change in the composition of the analysed samples is often observed (e.g. aromatic and medical active plants: Bicchi et al., 2000 or fruit juices: Widder and Eggers, 2001). The aim of this study was therefore to find the right type of fiber which can extract qualitatively and quantitatively all aroma-active compounds from *D. edulis* which are responsible for the characteristic and pleasant odor impression.

"African pears" – Fruits of the baobab tree*

- HS-SPME, GC-FID and GCMS in pulp aroma analysis
- Qualitative and quantitative analysis of aroma-active compounds in fibers
- 4 components (out of 40) identified being responsible for the aroma impression

Sample preparation

Dacryodes edulis fruits were bought at a local market in Ngaoundere (northern Cameroon) in September 2002, immediately after the harvest. The species identity was confirmed by a local botanist, and the control specimen was deposited at the National Herbarium of Yaoundé.

The samples investigated were prepared from a total of 5 fruits which were peeled and the pulp separated from the stone using a commercial stainless steel knife.

The pulp (300 g) was portioned in 5 x 60 g samples and each was placed in a 240 mL flask (Supelco Co., product no. 23231), olfactorally evaluated by professional perfumers (Dragoco Co., Vienna, Austria, now Symrise) and afterwards closed with hole caps (Supelco Co., product no. 23237) with Teflon/silicone septa (Supelco Co., product no. 23245-U).

The pulp samples were heated in a water bath at 40 °C for 1 hour and the volatiles extracted by solid-phase-microextraction from the headspace with the following fibers: 50/30 mm DVB/Carboxen/PDMS on a 2 cm Stable-Flex coated glass fiber (Supelco 57348-U), 50/30 mm DVB/Carboxen/PDMS-Stable-Flex fiber (Supelco 57328-U), 70 mm Carbowax/DVB-Stable-Flex fiber (Supelco 57336-U), 65 mm PDMS/DVB Stable-Flex fiber (Supelco 57326-U) and 85 mm Carboxen/PDMS Stable-Flex fiber (Supelco 57334-U).

GC-FID and GCMS analysis

Subsequent desorption of the analytes took place in the hot injector (250 °C) of the GC-14 (FID: 320 °C) or GCMS-QP-5000 respectively. For the GC-FID measurements the carrier gas was hydrogen. ➧

Compound	RI	S-1[1]	S-2[2]	S-3[3]	S-4[4]	S-5[5]	Aroma impressions
Dimethyl sulphide	309	0.3	0.1	0.4	0.4	0.2	sharp, Allium-like
Ethanol	503	tr[6]	nd[7]	0.5	0.2	0.1	etheral, alcohol-like
2-Butanol	590	0.2	0.1	0.7	0.2	0.1	medicinal, etheral
Hexanal	801	tr	0.1	0.1	0.2	0.2	fatty, grassy, green
2-Methyl butanoic acid	837	0.8	0.7	1.3	0.9	0.6	fruity-fatty, spicy
(Z)-3-Hexen-1-ol	861	tr	tr	0.7	0.5	0.2	green ("leaf alcohol"), fresh
Hexanol	865	0.1	tr	0.6	0.4	0.2	alcoholic, ethereal, medicinal
Heptanal	899	tr	0.1	0.2	0.1	tr	fatty, sweet, woody, nutty, fruity
α-Thujene	925	0.1	0.1	0.3	0.2	tr	herbal, green
α-Pinene	934	59.8	59.1	47.1	55.6	60.5	woody, pine-like
Camphene	946	1.4	1.6	2.1	1.7	1.6	fresh, camphoraceous
Isoamyl propionate	952	0.6	0.5	0.8	0.3	0.2	fruity, pineapple-like
Sabinene	974	1.4	1.6	2.1	1.5	1.5	spicy, warm-woody
β-Pinene	981	8.0	7.9	6.7	7.7	8.2	woody, pine-like
Myrcene	989	14.2	13.9	12.9	14.0	14.8	sweet-balsamic, plastic-side-note
α-Phellandrene	1004	0.2	0.5	0.4	0.3	0.3	minty, herbal, spicy
δ-3-Carene	1011	0.3	0.2	0.1	0.2	0.2	sweet, refined limonene-note
π-Cymene	1027	0.5	0.7	0.5	0.4	0.2	weak citrus-note
Limonene	1031	3.8	4.0	3.4	6.4	4.3	citrus-, lemon- and orange-note
α-Terpinene	1034	0.1	0.2	0.1	0.2	tr	terpene-like
β-Phellandrene	1036	0.1	0.1	tr	0.1	tr	herbal, spicy
1.8-Cineole	1038	tr	0.1	tr	0.6	tr	fresh, eucalyptus-like
(Z)-β-Ocimene	1040	tr	nd	nd	0.1	nd	spicy (estragon- and basil-notes)
(E)-β-Ocimene	1048	tr	nd	nd	0.1	tr	spicy (estragon- and basil-notes)
γ-Terpinene	1061	tr	0.1	0.1	tr	tr	herbal, citrus-note
Terpinolene	1090	tr	0.1	0.2	tr	tr	sweet-piney, slightly sweet-anisic
Linalool	1101	0.1	0.1	1.3	tr	nd	floral, citrus-lemon-orange notes
Nonanal	1104	nd	0.1	0.8	nd	nd	fatty, waxy
2-Phenyl ethyl alcohol	1116	1.9	1.8	2.3	1.7	1.9	floral, rose-note
(Z)-Pinocarveol	1139	1.2	1.2	2.5	1.0	1.0	camphoraceous
Verbenol	1178	1.8	1.7	3.1	1.6	1.9	minty, spicy
Terpinene-4-ol	1183	0.4	0.5	2.4	0.1	0.9	spicy, woody-earthy, liliac-notes
α-Terpineol	1198	0.4	0.3	1.1	0.2	0.8	liliac odor, floral, fruity
Decanal	1204	tr	0.1	0.6	tr	tr	sweet-waxy, floral, citrus-note
Verbenone	1215	tr	0.1	0.4	0.1	tr	minty, spicy
Carvone	1255	tr	nd	0.2	tr	nd	spicy, fresh, herbal
α-Copaene	1391	0.2	0.2	0.1	0.3	tr	woody, spicy
β-Caryophyllene	1437	1.1	1.1	0.7	0.6	0.4	terpene-odor, woody, spicy
Aromadendrene	1459	0.1	0.3	0.1	0.2	tr	woody, spicy
α-Humulene	1472	tr	0.1	0.1	0.1	tr	weak woody
Nerolidol	1565	tr	nd	0.9	tr	0.1	rose-, apple-, citrus-like green
δ-Cadinol	1658	tr	tr	0.6	0.1	nd	spicy
α-Cadinol	1675	tr	0.1	0.5	0.1	nd	spicy
Farnesol	1834	tr	nd	0.3	0.1	nd	floral-oily

S-1: 50/30 µm DVB/Carboxen/PDMS-2cm-StableFlex – **S-2:** 50/30 µm DVB/Carboxen/PDMS-StableFlex
S-3: 70 µm Carbowax/DVB-StableFlex – **S-4:** 65 µm PDMS/DVB-StableFlex – **S-5:** 85 µm Carboxen/PDMS-StableFlex
tr: trace compound (less than 0.1 %) – **nd:** not detected

Table 1: Headspace aroma compounds from the pulp of *Dacryodes edulis* fruits from Cameroon by using differently coated SPME fibers in order of their retention indices (RI) on a carbowax column in percentage (%-peak area, calculated from GC/FID analysis). Aroma impressions of identified headspace SPME pulp constituents from published data elsewhere (Arctander, 1969; Bauer et al., 1997; Fazzalari, 1978; Furia & Bellanca, 1975; Ohloff, 1994; Sigma-Aldrich, 2001).

The temperature programme was: 40 °C/5 min to 280 °C/5 min, with a heating rate of 6 °C/min. The columns were 30 m x 0.32 mm bonded FSOT-RSL-200 fused silica, with a film thickness of 0.25 µm (BioRad, Germany) and 60 m x 0.32 mm bonded Stabilwax, with a film thickness of 0.50 µm (Restek, USA). Quantification was achieved using peak area calculations in %, and compound identification was carried out partly using correlations between retention times (Retention indices according to Adams, 2001; Davies, 1990; Jennings & Shibamoto, 1980; Kondioya & Berdaque, 1996; Tudor, 1997).

For the GCMS experiments the carrier gas was helium; injector temperature 250 °C; interface-heating at 300 °C, EI-mode was 70 eV, and the scan-range was 41 - 450 amu. All other parameters were the same as for the GC/FID analysis. Mass spectra correlations were performed using Wiley, NBS, NIST and our own library as well as published data (Adams, 2001; Jennings & Shibamoto, 1980; Joulain & König, 1998).

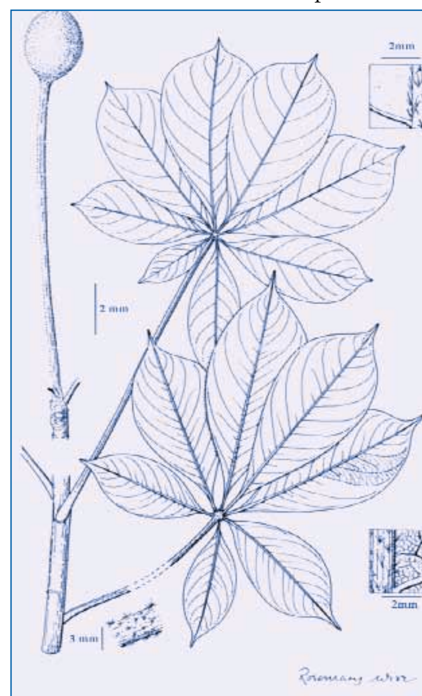
Results and discussion

The pulp samples of ripe African pear fruits from Cameroon were olfactorally evaluated by professional perfumers as follows:

pleasant warm-woody-balsamic (pinene-like), fresh-fruity (citrus-like), sweet-fruity (direction of ripe plum), weak minty-floral and in the background fatty and spicy aroma;

About 50 volatiles could be detected and more than 40 of them identified in the pulp headspace of *D. edulis*. Monoterpenes in particular, such as α-pinene (47.1 % - 60.5 %) myrcene (12.9 % - 14.8 %), β-pinene (6.7 % - 8.2 %) and limonene (3.4 % - 6.4 %) were found to be main compounds in the pulp headspace of *D. edulis* fruits (see Table 1)

Using correlations of analytical data with odor-notes of identified essential oil compounds

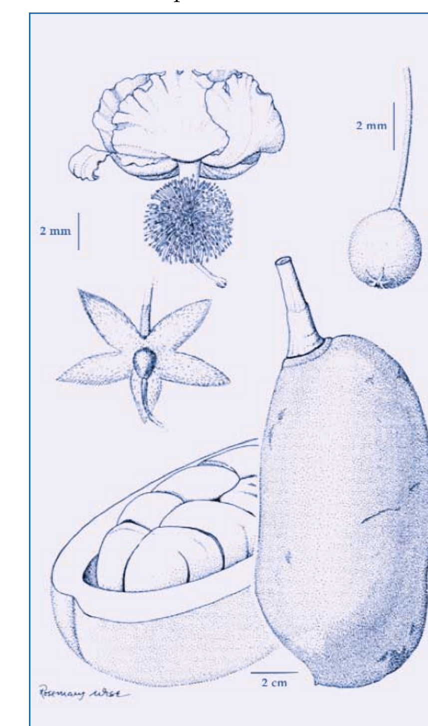


Leaf and fruit of the baobab tree

published elsewhere (Arctander, 1969; Bauer et al., 1997; Fazzalari, 1978; Furia & Bellanca, 1975; Ohloff, 1994; Sigma-Aldrich, 2001; see Table 1), we can deduce the following:

- dominating sweet-woody-balsamic odor impressions can be attributed to the main compounds α- and β-pinene as well as myrcene
- fresh-fruity (citrus-like) and sweet-fruity (direction of ripe plum) aroma notes are known from limonene, p-cymene, and some terpinene derivatives
- spicy odor possess some monoterpenes, such as sabinene, phellandrene and ocimene derivatives, and sesquiterpenes, such as aromadendrene and cadinols
- green and fresh (camphoraceous- and minty-note) odor impressions are characteristic for hexane derivatives (green-grassy), camphene, pinocarveol, verbenol, verbenone (fresh-minty) as well as linalool, Terpinen-4-ol and α-Terpineol (floral)

Comparison of the analytical results from the extraction with the different SPME fibers clearly shows that by using the DBB/Carboxen/PDMS/Stable-Flex Fibers all aroma active compounds in the headspace of African Pears can be identified and detected using GC-FID and GCMS analysis. Thus also all olfactoric impressions of the identified compounds can be correlated with the overall aroma of *D. edulis*. Using the 3 other fibers some compounds which add a considerable amount to the characteristic flavour of the pulp of African Pears could not be detected.



Summary

To summarize the investigation of pulp HS-SPME aroma compounds of *Dacryodes edulis* fruits from Cameroon with GC-FID and GCMS, we can report that α-pinene, β-pinene, myrcene and limonene are the main components among more than 40 compounds identified and mainly account also for the aroma impression of the African Pear. Other Headspace compounds are present in medium or low concentrations and also have some importance to the overall aroma. These main and minor compounds could only be extracted in detectable concentrations from the headspace of the African Pear by using the DVB/Carboxen/PDMS-Stable-Flex fibers.

This fiber was thus found to be optimal for the aroma compounds analysis of exotic fruits.

We acknowledge the olfactory evaluations and the advisory function for the smell correlations of Wolfgang Höppner and Volker Hausmann, chief perfumers of Dragoco Co., Vienna.

L. Jirovetz* and G. Buchbauera, Department of Pharmaceutical Chemistry, University of Vienna, Althanstr. 14, 1090 Vienna, Austria

M.B. Ngassoum, Department of Applied Chemistry, ENSAI, University of Ngaoundere, BP 455, Ngaoundere, Cameroon

Laboratoire de Physicochimie et Gènie Alimentaire, ENSAIA-INPL, 2 Avenue de la Foret de la Haye, 54505 Vandoeuve les Nancy-Cedex, France

*For further information please contact:
Dr. Leopold Jirovetz
Tel.: ++43-1-42 77-55 091
Fax: ++43-1-42 77-95 51
Email: leopold.jirovetz@univie.ac.at

Customized solutions fo r complex GCMS problems

Determination of sulphur compounds in carbon dioxide

Figure 1 shows the complete set-up and figure 2 shows detail of the gas sampler

A large part of all GC applications concerns the analysis of gases, permanent gases and traces of impurities in these gases. For large concentrations, several detectors are available.

The vast majority is analysed with the Thermal Conductivity Detector (TCD) and in many cases a FID will also satisfy. If impurities in the gases are of interest, the sensitivity and selectivity of conventional detectors is not sufficient. More specialised devices could be used such as the Pulsed Discharge Detector, or in the case of Sulphur containing compounds, an FPD or Sulphur Chemiluminescence Detector. Robustness, linearity and ease of use hamper all three-detector devices.

For sensitive and selective trace analysis a mass spectrometer could be a good solution. In general the sensitivity of a GCMS is a factor of 1000 times higher than a conventional FID (picogram-range compared to nanogram-range). With the use of Single Ion Monitoring selectivity is excellent.

Sulphur trace analysis is extremely difficult because the low volatile compounds will stick to all metal surfaces throughout the complete instrumentation. As a result poor detection limits and severe memory problems can be expected.

In this article the instrumental set-up and method is described for the analysis of H_2S, COS and DMS (dimethylsufide) in carbon dioxide. The regenerated CO_2 is used for brewery applications and is not allowed to contain any remaining sulphur traces.

The system described here is a fully automated sulphur trace gas analysis system and for this purpose a sampler was developed which can contain 10 sample bags, each having a volume of 3 litres. Specially developed software controls the gas sampler and this software is adapted into Shimadzu's GCMSsolution software.

Instrument set-up

The gas sampler contains several switching valves and the sample is introduced into the GCMS via a loop/backflush valve. The sampler uses a 10-position selection valve. The Tedlar gas sample bags are connected to this valve via needles. The sample bags contain an adapter part with a septum. All of the samples are placed inside the sampler box, which can be closed with a cover. By applying a slight overpressure to the sampler box the sample is transferred to the sample loop.

The pressure in the sampler box determines the amount of gas flowing through the sample loop, an open-close valve is controlling the purge- and filling time of the sample loop. The timing of this valve is controlled by custom-made software. In this way purging and filling of the sample loop is easy and reproducible.

If sample bags of 3 litres are used, several samples can be taken from one bag and re-analysing the sample is no longer a problem.

The software is written as a "User Program" which can be incorporated within the batch in GCMSsolution. For this the "user program"-column is added to the batch table. In the "User Program" window the program file is entered and in "Parameter" a time (purge- and fill time of the loop) and a sample position is entered. The sample position in the active batch line now corresponds with the sample position in the sampler. There is no need to create different sample schedules although the sampler is an external device.

The sulphur compounds of interest, H_2S, COS and DMS, are volatiles, and larger, less volatile compounds are flushed back via a conventional back/flush system (6-port two position valve). This valve is mounted on top of the GC and separately heated. The analytical column is a GasPro fused silica (30 m x 0.32 mm ID) column, which has an excellent resolving power for volatile compounds.

A second flow line is used for the determination of volatile organic compounds. For this a Tekmar AreoTrap 6000 is used. The gas sample is now transferred from the gas sampler via a valve to the AreoTrap 6000 concentrator and subsequently transferred to a second column (75 m, 0.45 mm, 2.55 µm DB624). Typical compounds to be analysed are acetaldehyde, methanol, ethanol, iso-amylacetate and ethylcaproate.

The two analytical columns are mounted in a 4 port, two-position valve that is located just before the MS interface. This valve is a delicate part of the system due to the high vacuum level of the MS. A fused silica capillary restriction controls the final flow into the MS.

All components in the set-up are Cheminert treated or made of Teflon to prevent surface adsorption of the compounds to be analysed. Where possible, Teflon tubing is used.

Figure 1 shows the complete setup and figure 2 shows detail of the gas sampler.

Results

Figure 3 shows the calibration curve of COS in Carbon dioxide in the range of 30 to 500 ppb. Detailed information of the curve is listed below.

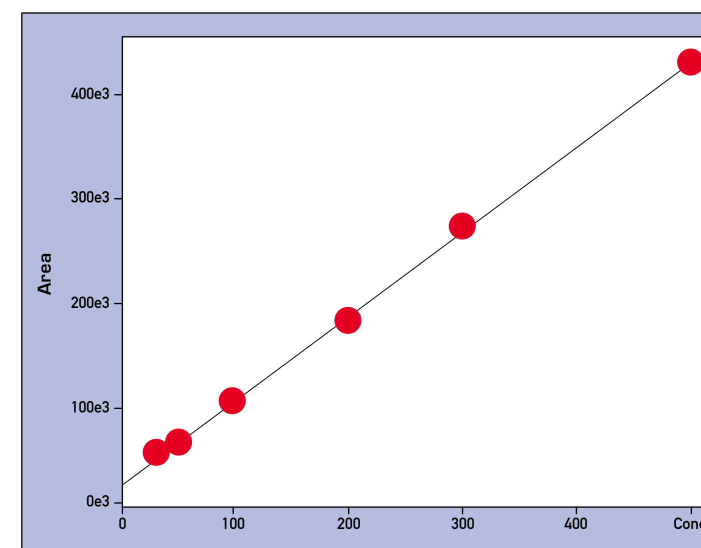


Figure 3: Calibration curves for COS in Carbon dioxide standards (concentration range 30 ppb to 500 ppb). For H_2S, the same concentration range was used. The R-coefficient was 0.9981. For DMS (range 9 to 700 ppb) the R-coefficient was 0.99998

Y = 836.7421X + 24931.29
R^2 = 0.9993579
R = 0.9996789
External Standard:
Curve: Linear
Origin: Not forced
Weighting Method: None
Mean RF: 1143.67
RF SD: 325.0274
RF % RSD: 28.41969

- Sulphur trace analysis is extremely difficult due to low volatile compounds
- Instrumental set-up and method for the analysis of H_2O, COS and DMS in CO_2
- Gas sampler software is adapted into GCMSsolution software

The calibration curves for H_2S, DMS and also the organic volatiles are very similar and correlation coefficients of 0.999 (or higher) are easily obtained. The limit of detection for sulphur containing compounds is:

20 ppb for H_2S, for COS and DMS 500 ppt and 1 ppb respectively. Detection limits with the Tekmar AreoTrap 6000 of 1 ppb are very easily obtained for all compounds. Reproducibility of 2 % is more than acceptable for gas analysis.

Figure 4 shows the quantitation window of a real carbon dioxide sample originating from a beer production plant. As can be seen, a substantial amount of COS is found, but H_2S is absent.

The method described below is only valid for the sulphur analysis. The standards were prepared and diluted with ultra clean carbon dioxide and stored in Tedlar sample bags.

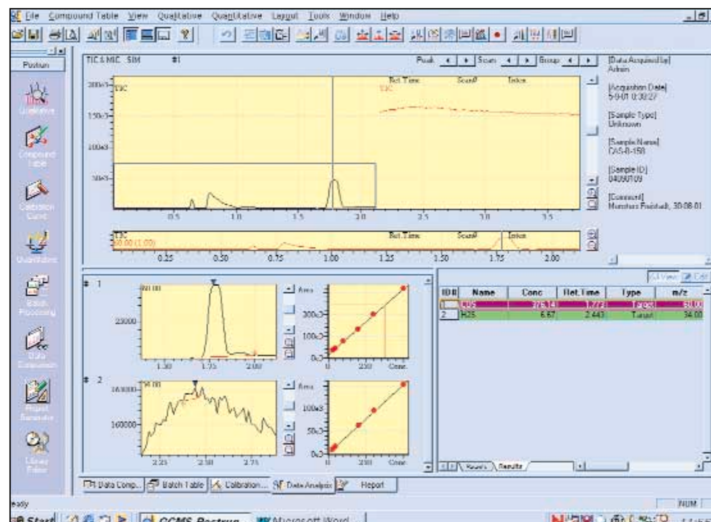


Figure 4: Quantitation window of a real sample obtained from a brewery. COS concentration is 243 ppb and H_2S level is less than 20 ppb. In the upper windows both the mass signals of COS and H_2S are visible. In the lower part the quantitation is depicted

Calibration samples:			
500 ppb standard	:	COS and H_2S each	727 ppb DMS
300 ppb standard	:	COS and H_2S each	381 ppb DMS
200 ppb standard	:	COS and H_2S each	99 ppb DMS
100 ppb standard	:	COS and H_2S each	18 ppb DMS
50 ppb standard	:	COS and H_2S each	9 ppb DMS
30 ppb standard	:	COS and H_2S each	

Conclusions

The obtained detection limit for H_2S, COS and DMS is 20, 0.5 and 1 ppb respectively. This is achieved with a 250 µL sample loop. Especially in case of H_2S, this is more than acceptable. In general sulphur compounds are very difficult to analyse.

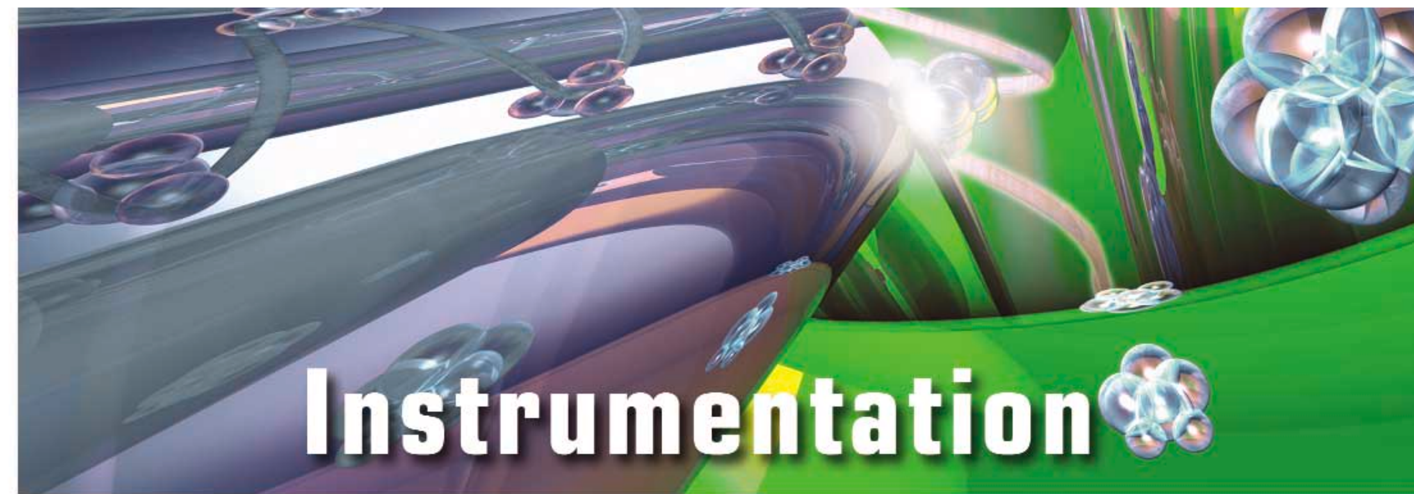
The use of Teflon tubing and parts, and the Cheminert treatment of several switching valves is necessary. The flexibility of the system for general gas analysis is proved by the fact that a Tekmar AreoTrap 6000 is also incorporated in the system.

The possibility of controlling the complete system with GCMSsolution makes this gas analyser a flexible, sensitive and selective tool for all kind of gases, with an optimal ease of use.

Method description

Equipment:
Autosampler: containing 10 Tedlar sample bags, each of 3 litre volume
GCMS: Shimadzu QP-5050A GCMS (with EI)
Column: GasPro fused silica 30 m x 0.32 mm ID
The gas chromatograph accommodates one 10-port 2-position valve, a 6-port valve and a 4-port valve for back flush and column switching purposes
The autosampler contains a 10-port multiposition valve and a 10-port 2-position valve
Tekmar AreoTrap 6000, second flow line. The column used is a 75 m, 0.45 mm 2.55 µm DB624
The software used to control the gas sampler is adapted to the Shimadzu GCMSsolution software

Chromatographic conditions:	
Gas loop temperature	: 50 °C
Loop volume	: 250 µL
Column oven	: isothermal 50 °C
Carrier gas flow (helium)	: 2 mL/min, constant flow
MS-parameters:	
Detector Volts	: 1.5 kV
Acquisition mode	: SIM (single ion monitoring)
Ion set 1	: M/Z = 60, acquisition time = 0.0 – 2.10 min
Ion set 2	: M/Z = 34, acquisition time = 2.10 – 3.75 min



One more success story

The GC prototype – built in 1957

■ GC-2010 offers superior precision in qualitative and quantitative analyses

■ Advanced Flow Control (AFC)

Five years after the first developments in the field of gas chromatography, Shimadzu presented the first GC prototype in 1957 at a conference of Japanese chemists. The interest was immense and made the debut of one of the first commercial gas chromatographs a world-wide resounding success. In the following months, Shimadzu had the "GC-1A" ready for production. This GC was much larger than current models and was initially used for the analysis of solvents, pharmaceutical and petroleum products.

From 1957 to now – lightening-paced development

With time, GCs were used for more and more applications and the column technology was improved. This meant that GC technology was soon in use in universities and in quality-control tasks, such as with the production of chemicals, pharmaceutical products and food.

In the following decades, the instruments became better and the range of accessories increased considerably. Some milestones of this development phase were such specific detectors as the electron capture detector (ECD), the thermoionization detector (TID), the photoionization detector (PID), the flame photometer (FPD) and the MS coupling. Later, the development of autosamplers progressed and the microprocessor technology rapidly increased the performance of the GCs. Nowadays, almost 20 years after the development of fused silica open tubular columns, capillary GC features in a growing proportion Fast-GC applications with Narrow bore columns.

State Of The Art: GC-2010

Forty years after the introduction of the first gas chromatographs, the current Shimadzu model – the GC-2010 – offers superior precision in qualitative and quantitative analyses, is fully automated and easy to use.The development of Advanced Flow Control (AFC) was an important factor in reaching this performance level. The unique constant linear velocity mode of the GC-2010 enables the user to work always under optimal flow conditions for highest resolution efficiency (van-Deemter minimum). Pressures up to 970 kPa and detector frequencies of 250 Hz with filter time constants of minimum 4 ms for all detectors (FID, ECD, FTD (NPD), FPD, TCD) make the GC-2010 the only GC on the market fully equipped for High Resolution Fast-GC.

GC: A proven method just keeps on getting better

Gas chromatography has established itself in the last 40 years as a reliable analytical method. New challenging applications and further developments as a result of research and development have also meant that the GC systems have kept on getting better.

This ensures that gas chromatography will continue to play an important role in instrumental analysis in the future.

GC-2010

Innovative design for the highest demands

The quadrupole mass spectrometer QP2010 meets the highest standards with respect to sensitivity, flexibility and reliability.

The differentially pumped vacuum system (250 x 65 L/s) and the ion source and detector guarantee maximum sensitivity (1 pg OFN S/N > 60).

A maximum level of flexibility

The optimisation of analytical results requires a high degree of flexibility. Via the separately heated ion source and the variable ionisation energy, all analytical parameters can be tuned exactly to the sample requirements. The wide mass range (1.5 - 1024 amu) allows the analysis of a broad sample range.

The GCMS-QP2010 allows the installation of all column types, from minibore (0.1 mm internal diameter) for Fast-GCMS up to wide-bore (0.53 mm internal diameter). Integrated in the QP2010 is the GC-2010. Its innovative injection system and the AFC-H (High Pressure Advanced Flow Control) offers the highest reproducibility for all application ranges. In the "Constant Linear Velocity" mode the resolution is optimised over the entire chromatogram. Together with the high scan rate of the mass spectrometer (10,000 masses per second) the QP2010 is optimally equipped for Fast-GCMS. The flexibility of the system is even further increased through the possibility to install an additional detector (FID, ECD, FTD, [NPD], FPD, TCD) which is also controlled via the GCMSsolution V.2 software. GC detector and MS data can be simultaneously acquired in order to confirm the sample results.

Security made easy

The quality of the results is assured via the quality control-, troubleshooting- and maintenance functions in accordance with GLP/GMP guidelines in the GCMSsolution V.2 software. The user is supported via the MSnavigator. User administration ensures that there is no unauthorised access to the system. All actions of the GCMS system are documented in the audit trail for verification at any point in time. Naturally, all statistical parameters can be determined directly using the GCMSsolution software. A quality report can be obtained directly in html format.

Not only quality control, but also routine daily use of the QP2010 is supported optimally via the GCMSsolution software. The "Assistant" menu bar allows direct access to all important software functions. Method parameters, batch and compound tables are easily set up via the "Wizard" function, which guides the user step by step through the individual menu options. The "Grouping" function allows easy analysis of homologous series. Reports can be formatted freely according to user requirements. The AOC-20i/s and AOC-5000 autosamplers are controlled directly via the software.

The GCMS-QP2010

■ Quadrupole mass spectrometer meets the highest standards regarding sensitivity, flexibility and reliability

■ Wide mass range

■ Installation of all column types

■ Quality control and routine analysis

Handy helper for GC and GCMS

The autosampler AOC-5000

The GCMS-QP2010 with autosampler AOC-5000

- Different sampling methods combined in one system
- Productivity meets accuracy
- Large volume injection

AOC-5000 is the highly flexible sampler for GC/GCMS analysis. This sampler combines liquid sampling, headspace- and solid-phase micro-extraction (SPME) technologies in one system. Changing between the different sampling modes is surprisingly easy: a simple exchange of the syringe makes it a snap.

The design of the AOC-5000 is based on a x-y-z robot arm. This arm moves rapidly and accurately to samples, wash ports or incubator. The position of the objects (injectors, trays, incubator.) as well as the sampling steps can be freely defined. In this way, parameters such as sucking and injection velocity or the variable needle-immersion depths in the injector and sample vial can be specified according to the application.

High productivity with maximum accuracy

In the headspace mode, equilibration- and syringe temperatures may be defined and flexibly programmed. The syringe is purged automatically with pure purge gas. The AOC-5000 can accommodate up to 96 sample vials of 10 or 20 mL. Six positions in the incubator allows parallel processing of the ongoing analysis with the equilibration (temperature + rotation in the incubator) of the next sample.

This feature guarantees high productivity at maximum analytical accuracy, due to the fact that the sample is only sucked when the analysis of the previous sample is completed and the GC has returned to its “ready” status. This type of communication between the GC and the sampler makes it possible to install cryogenic focussing of headspace samples onto the column. Syringe sizes from 1 to 5 mL offer maximum flexibility for the assorted applications.

Large volume injections

In the liquid mode, additional syringe rinses, using 2 different solvents, can be defined before and after the injection. The different syringe sizes also allow a wide range in injection volumes up to “large-volume injection”. The AOC-5000 can accommodate up to 600 sample vials of 1 mL. The individual injection cycles are correspondingly short, which is particulary important for “Fast-GC” applications.

Solid phase microextraction (SPME) has established itself as an alternative sample preparation mode for gas chromatography. This method reduces sample preparation time and makes the use of large amounts of solvent unnecessary. During SPME the sample is adsorbed onto a stationary phase on the SPME needle and subsequently desorbed in the GC injector. SPME increases the sensitivity through accumulation and is used in many applications such as environmental-, forensic-, food- and pharmaceutical analysis.

Cooled PTV injector Optic 3

Enhanced applications for GC and GCMS range

GC injection system Optic 3

- Versatile injection tool
- Perfect for applications where sensitivity is key issue
- Software for easy operation

The Optic 3 injector is a versatile tool for the Shimadzu GC and GCMS product range. It can be operated with split, splitless, on-column/AT-Column, DTD (Thermodesorption)/DMI (Difficult Matrix Introduction) and large-volume injections.

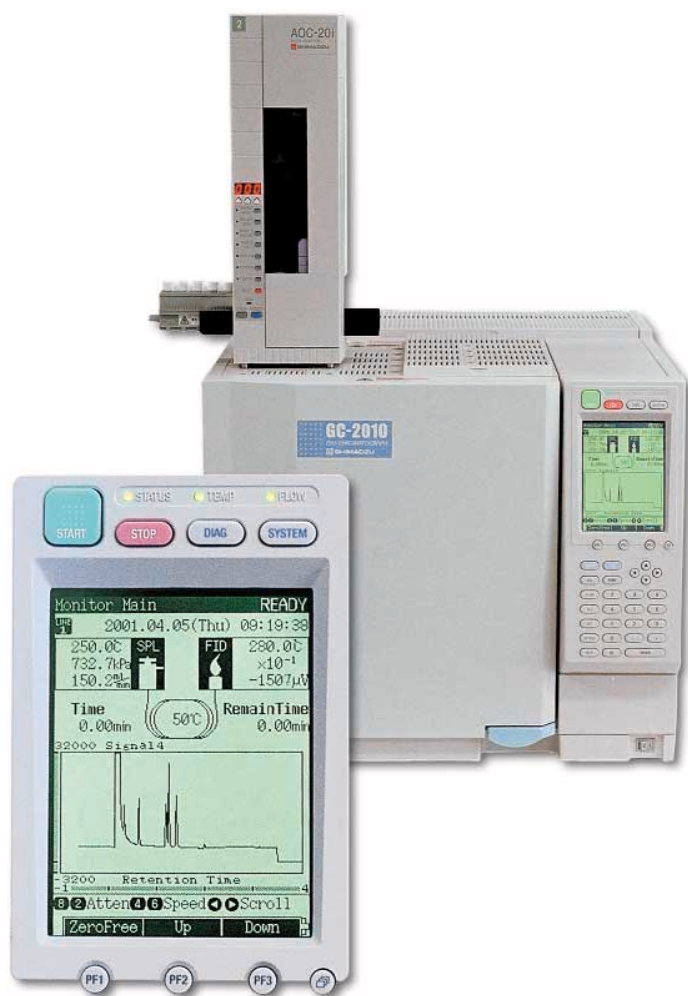
The designed software makes it easy to operate. The injector shows no discrimination and low thermal degradation of the sample.

By cooling the Optic 3 injector, compounds which would normally degrade in a hot injection port, e.g. thermally labile pesticides as well as highly volatile compounds, can be analysed without any difficulty. The temperature range of the Optic 3 is from ambient temperature + 10 °C to 600 °C (optionally between – 150 °C and 600 °C), making it very flexible.

A large array of liners is available for the Optic 3, which are easy to change, giving the user the choice for every application.

The application of large-volume injection leads to better detection limits and can be used in all application fields where sensitivity is the key issue, e.g. environmental or food analysis.

In addition the Optic 3 can be used for Thermodesorption analysis (DTD). It is also ideal for samples containing active and/or high boiling point compounds. Optionally available μ-vials, to be inserted inside the liner, allow the analysis of compounds directly from solid or heavily matrix loaded samples (DMI).



E^3-Concept: Efficient, Excellent, Easy

The GC-2010: Three times more productive, five times more sensitive

- Fast-GC analysis
- High productivity through AFC
- Excellent performance in reproducibility by injection system

The GC-2010 from Shimadzu offers the future of gas chromatography. It is specially designed for Fast-GC analysis providing high productivity through efficient analysis by an advanced flow control (AFC) of the third generation for high pressure (970 kPa) and high split ratios as standard, with the upmost sensitive detectors with fast sampling time, high power oven and high speed cooling oven capability. Thus it can double or even triple the productivity of conventional instruments.

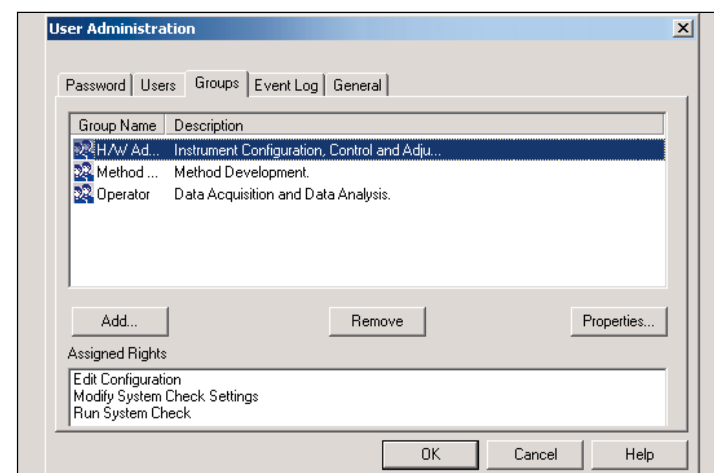
Excellent analysis results

Excellent performance in reproducibility of data is achieved by the injection system (even for solvents with large vapor volumes such as acetone) and highly sensitive detectors which support a wide range of applications. All detectors are conveniently located just inside the top cover. The flame photometric detector (FPD) provides 4 to 5 times more sensitivity than conventional modes. The ECD delivers ultra high sensitivity at 8 fg/s.

Easy operation and intelligent system suitability functions

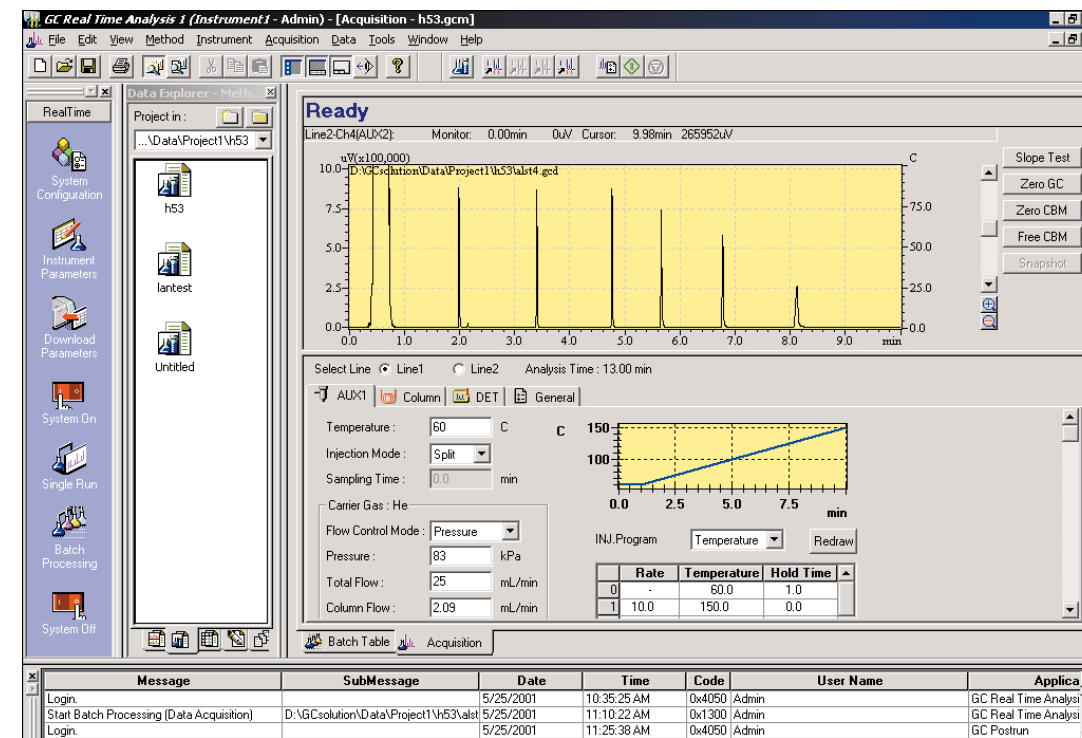
Operation is made easy by the large LC-display integrated which shows the current chromatogram and the analysis parameters thus enabling users of all levels to easily set up and operate the system.

The self-diagnosis functionality of the GC-2010 can maximize uptime of the GC system and provides documentation for validation purposes. Self-diagnosis functions include: septum and insert condition, temperature sensor check, DC voltage and AD converter. For validation purposes a log function records the history of the instrument and operational conditions including deviation from set parameters, changes of parameter settings and errors.

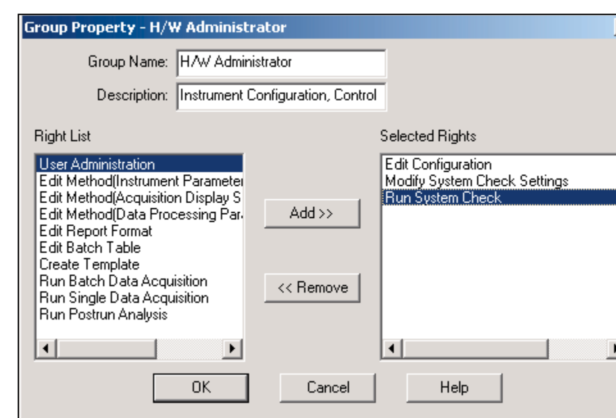


LabSolutions series GCsolution software

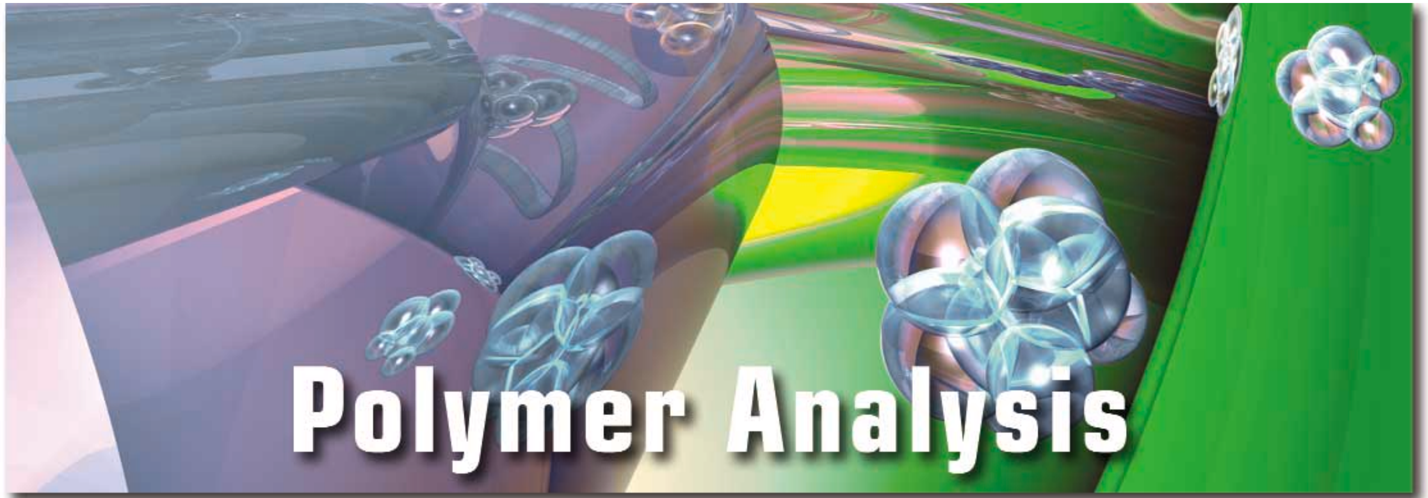
The GCsolution workstation is part of the LabSolutions software series. It provides the user with efficient and flexible tools for obtaining secure analysis results. As a true 32 bit software the GCsolution can be operated under Windows NT, 2000 and XP. Ease of operation is given by the assistant bar with all major functions at one glance as well as the wizard functions for method development and the flexible report generator. For working in a GLP/GMP environment it gives full support including pass word protection, audit trail and data integrity.



GCsolution: GC Real Time Analysis



GCsolution: Creating of usergroups and assignment of rights


Polymer Analysis

Not just clean – but pure...

Identification of inclusion compounds in paper using Pyrolysis-GCMS

Dirk Hinzmann, Papierfabrik Schoellershammer, Düren

- **Pyrolysis-GCMS is a universally applicable technique in quality control**
- **It helps to modify the paper production process**

Pyrolysis-GCMS is a universally applicable technique in quality control. Small sample amounts (< 500 µg) are sufficient to characterise a sample. The sample is placed in an inert gas stream at high-temperature whereby sample components are vaporised or decomposed.

These decomposition products formed are known as pyrolysis fragments. As they are present in the gas phase, they can be separated by gas chromatography (GC). Using a mass spectrometer (MS) as GC detector, each pyrolysis fragment will provide a specific mass spectrum and can be identified.

Optimisation of the production process

The aim of the study presented here was to characterise small dark inclusions in technical drawing paper. If the type of inclusions is known, it is possible to avoid the formation of such inclusions by a modification of the paper production process. Using a scalpel, the inclusions were cut out from the paper and placed in a platinum sample pot. This was placed in the pyrolysis oven and the analysis begun.

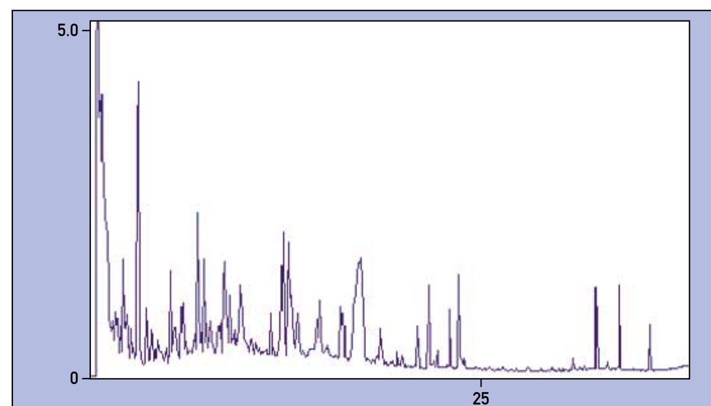


Figure 1: Pyrogram of the inclusion

Figure 1 shows the pyrogram of an inclusion sample. For comparison, the pyrogram of a "clean" paper spot is shown in Figure 2. In Figure 3 the automatic comparison of the two pyrograms shows a deviation in retention time range from 21 to 24 minutes.

A comparison of the determined mass spectra of these signals with a MS library (NIST 98) resulted in identification of the inclusion components as fatty acids (e.g. stearic acid, palmitic acid, see Figure 4). As sodium stearate was used during the production process, the inclusion components could be unequivocally assigned. Thus, by optimisation of the production process the future occurrence of these types of inclusions in paper products can be avoided.

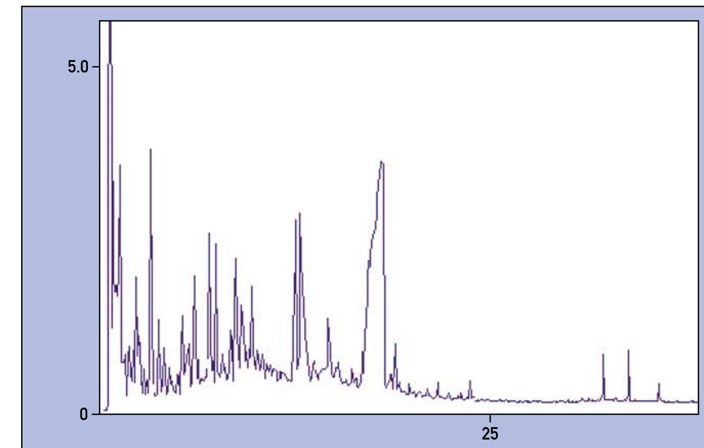


Figure 2: Pyrogram of the "clean" paper

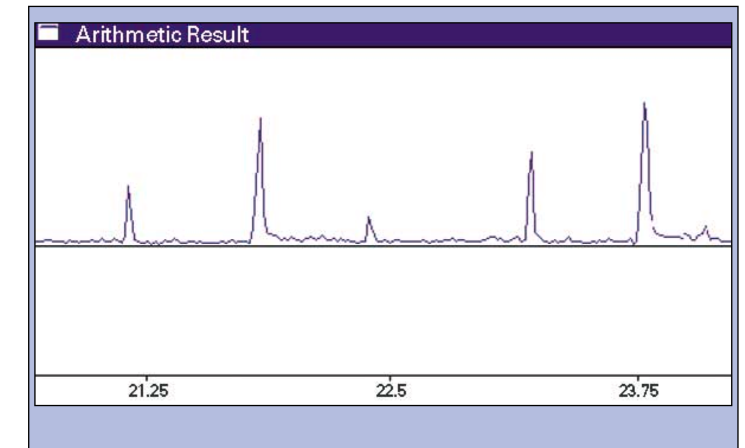


Figure 3: Differential pyrogram (insert minus "clean" pyrogram)

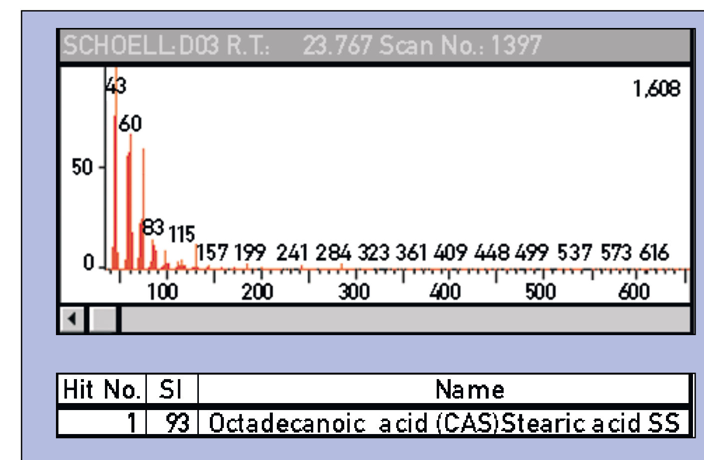
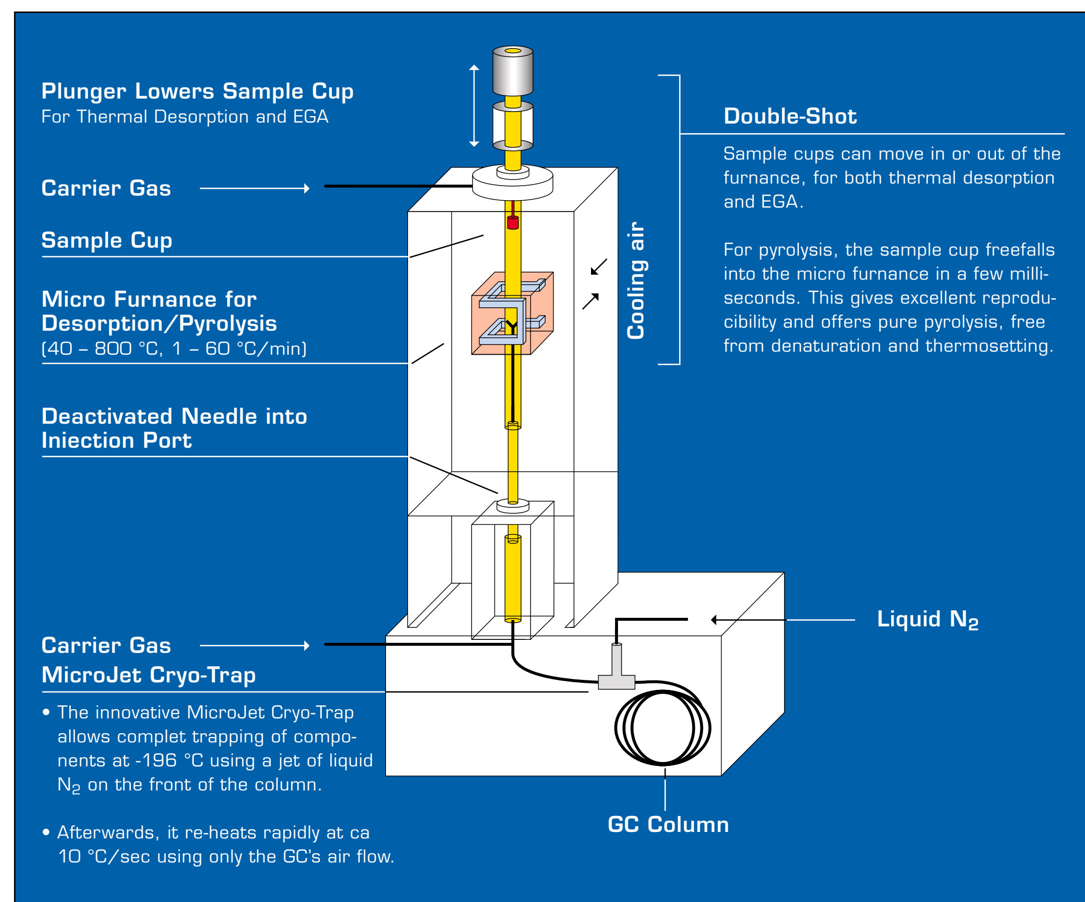


Figure 4: Identification of stearic acid (retention time 23.8 min)

All inclusive

Analysis of polymers made easy with the Py-2020iD Pyrolyzer and GCMS-QP2010



The sample holder decomposes in the furnace. The sample is then immediately pyrolysed

The Py-2020iD Pyrolyzer from Frontier Lab combines all of the features expected for a comprehensive analysis of polymer samples. The specialised furnace design provides highly reproducible pyrolysis and characterization of polymer samples. The 2020 is closely coupled to the GC, with a completely inert sample path, so there is no loss of compounds at active sites or cold spots.

Two powerful techniques:

Double-Shot Analysis

Double-Shot is the unique combination of *Thermal Desorption* and *Pyrolysis*. It can be used for volatile compounds in polymeric materials first, and then for the polymer itself. *Thermal Desorption* allows analysis of volatile compounds in polymers such as residual solvents, monomers and additives such as antioxidants and stabilizers. Then the users can go directly to Pyrolysis without needing to load a second sample. *Pyrolysis* handles macromolecular and other non-volatile components. GC separates the thermally fragmented species, and MS identifies them. With Pyrolysis polymer blends can be analysed and microstructures identified such as terminal groups. As shown below, the sample cup free-falls into the furnace. In a few milliseconds, the sample is pyrolyzed with excellent reproducibility.

Evolved Gas Analysis (EGA)

EGA allows on-line MS analysis of compounds evolved from the polymer over a wide temperature programming range. The users can see which zones of the EGA profile need to be collected in heart-cuts for further analysis. Any desired zone of the EGA thermogram can be collected automatically as a heart-cut and introduced into the GCMS.

Identification using GCMS

The Frontier Lab EGA & Pyrogram libraries and search algorithm bring new capabilities to the Shimadzu GCMS-QP2010. Now users can take advantage of all available data and identify unknown polymeric material rapidly and specifically.

- System includes all features for comprehensive analysis of polymer samples
- Double-Shot analysis
- Evolved Gas Analysis (EGA)
- Library helps to identify unknown polymeric material rapidly and specifically

Saving time in Pyrolysis-GCMS

Fast-GC columns reduce measuring time

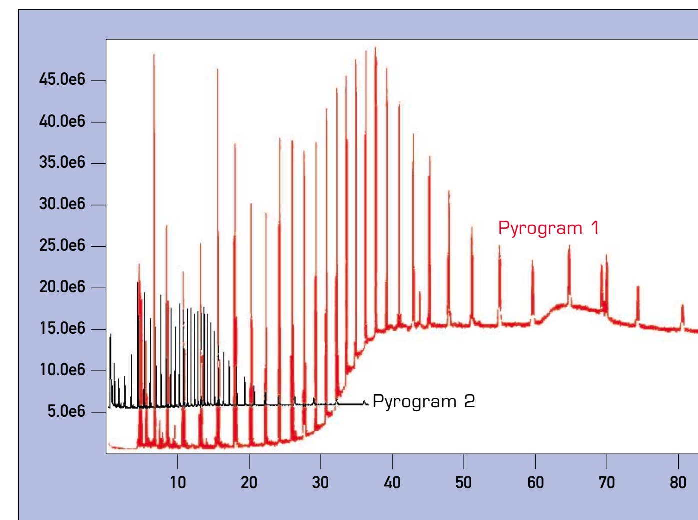
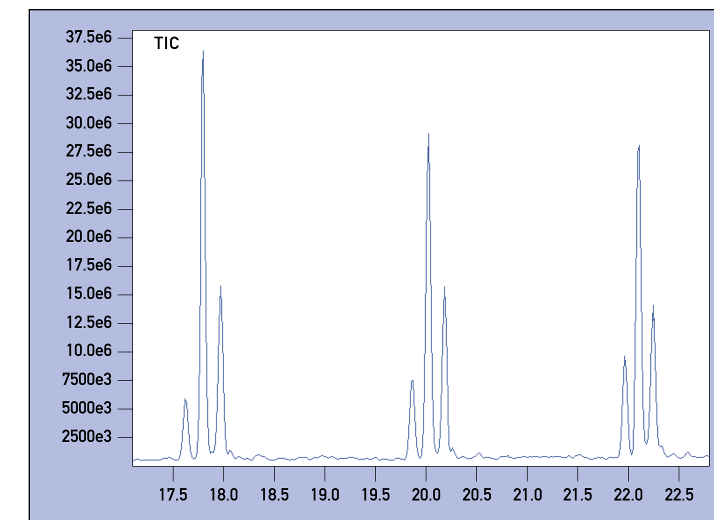
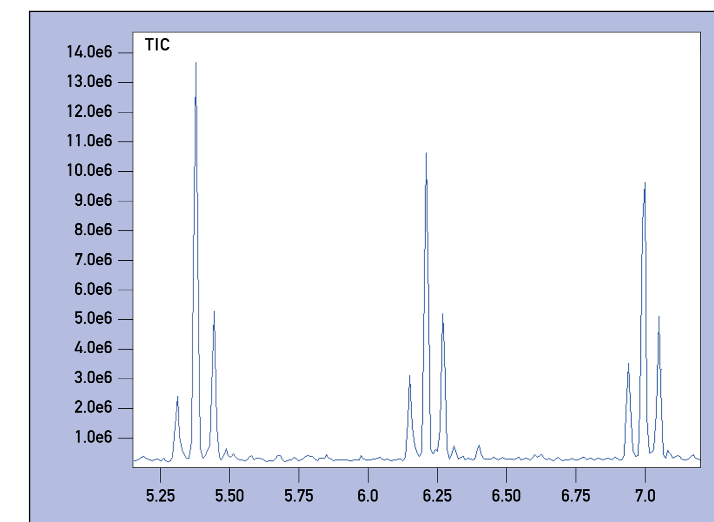


Figure 1 demonstrates the drastic saving in time (more than 40 minutes!), which is obtained by using a fast 10 m GC column, (0.1 mm ID, 0.4 µm film thickness; see pyrogram 2) compared to a standard 60 m pyrolysis column (0.32 mm ID, 1 µm film thickness; see pyrogram 1)



Figures 2 and 3 represent the last baseline separated polyethylene triplets



Everyone, who has had experience with Pyrolysis-GCMS, has occasionally been complaining about long analysis times. Depending on the type of samples, these can take up to two hours per run. Fast-GC, which is now considered the “state of the art”, has increased sample throughput and productivity in gas chromatographic analysis.

In contrast to conventional chromatography, Fast-GC uses shorter high-performance columns with a smaller internal diameter. The smaller column diameter keeps the separation efficiency high, while analysis times are considerably reduced compared to longer columns.

Fast-GC, however, makes special demands on the GCMS system. An important requirement for obtaining optimum results are the high scan rates (10,000 amu/s, aquisition frequency 50 Hz, for GCMS-QP2010) needed to obtain enough data points per peak in order to guarantee reproducible results during library searches and quantification. In addition, higher heating rates, faster cool-down as well as the possibility to work with extremely high column backpressures, play a decisive role. And last but not least, the quality of the capillary columns is of utmost importance. Due to the applied high heating rates in Fast-GC, low-bleed stationary phases must be employed.

A one third decrease in time

Fast-GC columns can also be applied in Pyrolysis-GCMS and analysis times can be drastically reduced. An example is the analysis of a polyethylene sample: the retention time of pyrolysis fragments of the polyethylenes can be reduced by one third, without loss in resolution of the polyethylene triplets.

- Fast-GC is state of the art
- High separation efficiency, reduced analysis times
- High scan rates

Py-GCMS in polymer and additive analysis

Pyrolysis-GCMS in use

Polymers are part of everyday life. They are used in an ever-growing number of applications, and new types of polymers and additives of increased quality are continuously being developed for new applications.

The development of new analytical methods runs parallel to the characterisation of these new polymer products. At DSM Research in Geleen, the Netherlands, pyrolysis-gas chromatography/mass spectrometry (Py-GCMS) is used for the analysis of polymers and additives.

In Py-GCMS the sample is thermally fragmented in the pyrolyser in a helium atmosphere; the fragments are then separated in the gas chromatograph and subsequently detected in the mass spectrometer. The identity and amount of the fragments can be determined and in this way the original composition of the unknown sample can be deduced.

At DSM Research a Py-GCMS data bank was set up for polymer as well as for additive fragments. This way Py-GCMS can be used as a screening method.

Clear advantages of Py-GCMS are that no sample preparation is needed and it is possible to analyse very small sample amounts (approx. 0.05 mg). In principle all organic materials, which can be fragmented into volatile products or which can be vaporised intact at temperatures up to 800 °C, may be analysed using Py-GCMS.

The fact that this is applicable to most polymers and additives is reflected in the wide application range for Py-GCMS:

- copolymers and polymer blends (for example impact modifiers)
- cross-linked polymers (for example vulcanised materials, resins)
- oligomer additives which are otherwise difficult to extract (for example flame retarders, antioxidants)
- samples with inorganic components (for example fibre optics, fillers)
- contaminated samples (for example contaminants, residues).

- **New type of analysis for new types of polymers**
- **No sample preparation needed**
- **Applicable to most polymers and additives**

LabSolutions – Solutions for your laboratory

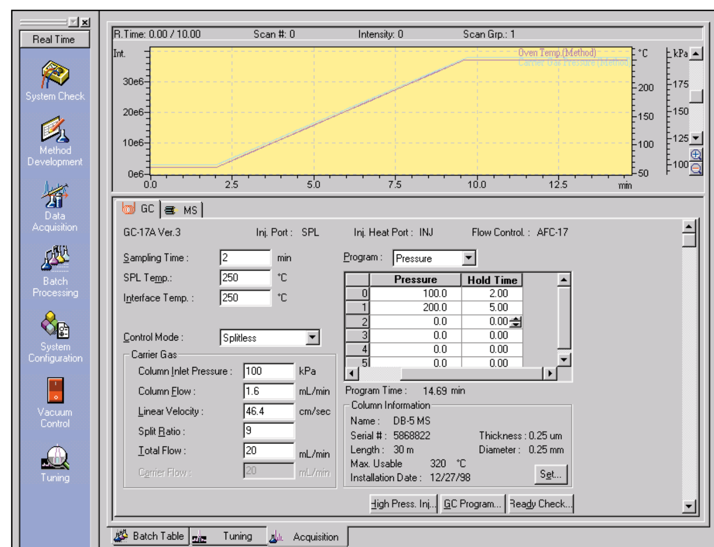


Figure 1: Intuitive software operation via icons

- **LabSolutions software series combines required functionalities and customer specific formats**
- **Integrity of recorded data**
- **Hierarchy of access privileges**
- **Flexibility, user-friendliness, efficiency**

LabSolutions, the software series for Shimadzu's chromatography systems, offers additional functionalities such as GLP-/GMP support, validation functions and design of custom report formats.

This means: greater flexibility, increased user-friendliness and higher efficiency. All major functions of the software can be used intuitively via icons.

Individual desktop adaption

The desktop can be adapted according to the specific user needs, with different pop-up windows for instance peak monitor or batch tables. The settings will be stored, also after completing the analysis and are activated at the next system start-up. Important for every user is the integrity of the recorded data. Data integrity is safeguarded by the project files, which contain all relevant data such as method parameters, chromatograms, batch tables and calibration curves.

High user-friendliness

Method development, batch processing and quantitation is simplified via wizard functions, which guide the user through the parameters step-by-step. The results of the analysis can be printed out in a user-specific report format. The corresponding icons are activated in a task list and are embedded in the report by a mouse click; for example chromatogram, library search or peak table. It is also possible to freely select the placement and size of the individual report components.

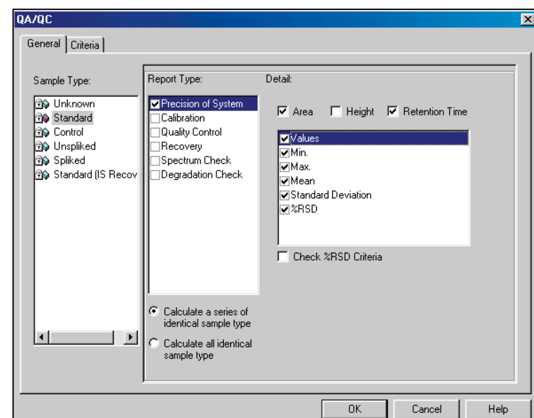


Figure 2: Integrated validation functions

Integrated validation functions

The integrated validation functions simplify compliance with the GLP-/GMP guidelines. Data security is offered by the various user-levels. For each level it can be decided which access privileges a particular user has to the software, from simple technician to system administrator.

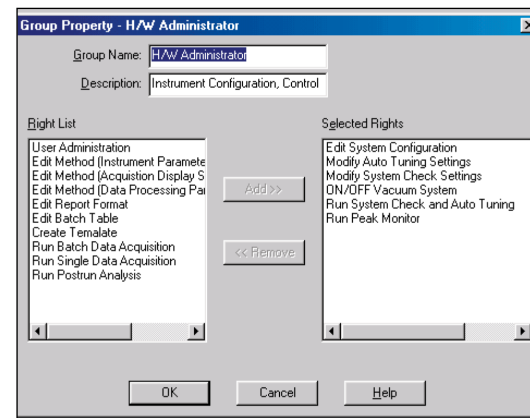
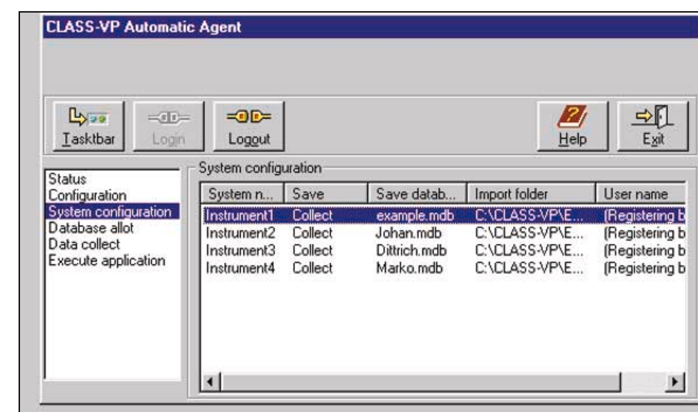
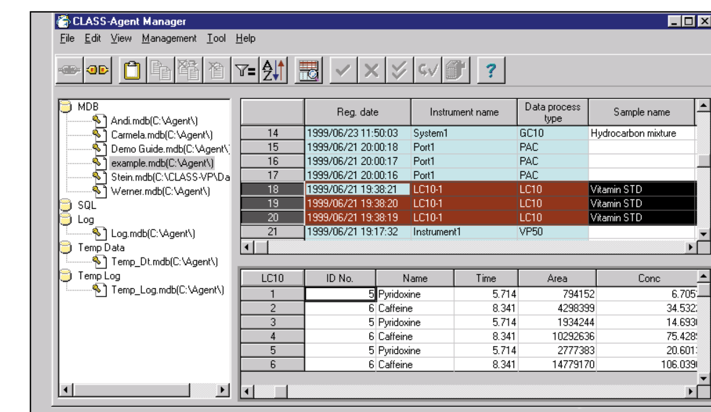


Figure 3: Classification of user privileges

Of course, all levels are secured via passwords. The audit-trail, which documents all actions, allows easy tracing of system use.


Automatic registration of data in the database


Extensive data search facilities

One for all – All for one

The CLASS-Agent software

The CLASS-Agent database connects Shimadzu's analytical instruments to a laboratory network. Data from various different analytical instruments such as HPLC, LCMS, GC, GCMS, TOC, Spectroscopy, Chromatopac and balances can be registered automatically into the database. All relevant information such as analytical methods, date and time of data acquisition, name of the operator and chromatograms can be stored and archived. In the network a central server can subsequently administer all data.

The CLASS-Agent database software distinguishes itself by the following features:

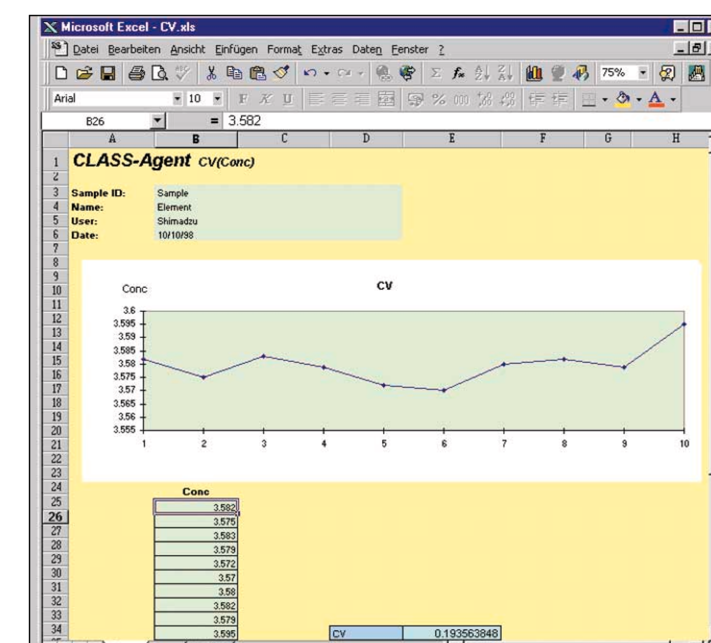
- Simple management of large quantity of data over a longer time interval
- Fast data searching according to specific and selective criteria (sample name, registration date, user etc.)
- Direct compatibility with Excel and Word
- Simple interface with various analytical instruments
- Broader security functions according to GLP/GMP standards
- Support of Access- and SQL server formats
- Flexibility from stand-alone to client/server type.

After analysis, e.g. GC results obtained with CLASS-VP 7.2 are automatically entered into the database by the CLASS-VP Automatic Agent. Using a database allot key (sample ID, user name and comment), the data can be stored in a project-specific database. Chromatograms, methods, sample tables and AIA files are archived together in a compressed file. This efficient data archiving procedure allows data decompression and re-evaluation at all times. Using the CLASS-VP manual agent, data can be entered into the database also at a later date.

Database searches with the CLASS-Agent manager

When searching through the database, the Agent Manager can search according to date, user, sequence, sample ID, comment etc. The search can be narrowed down to data on single peaks such as retention time, concentration, plate number etc. and can be listed in a table. These results can be copied into pre-defined Excel spreadsheets and can be further analysed statistically or represented as graphs or directly printed from the CLASS-Agent.

The integrated validation functions simplify compliance with


Representation of the results in pre-defined Excel spreadsheets

the GLP-/GMP guidelines. Data security is offered by the various user-levels. For each level it can be decided which access privileges a particular user has to the software, from simple technician to system administrator.

GLP/GMP compliance is effected via different user levels, automatic logbook functions and complete 21 CFR Part 11 compatibility.

- **Software integrates single analytical instruments in a laboratory network**
- **GLP-/GMP compliant**
- **21 CFR Part 11 compatibility**

Automation utilising LabSolutions software

- **Analysis with just a few mouseclicks**
- **Extra information remains in the background**
- **OLE interface is key to access internal functions of the software**

What is true for every software package also applies to routine analysis: often only a fraction of the possibilities of modern instrument software are actually used. As today's software offers a wealth of information and functionalities, sufficient technical know-how and sometimes long training periods are needed.

How useful it would be if an analysis could be started with just a few mouse clicks while extra information remained in the background. Sometimes special evaluation functions or automatic data transfer functions to a LIMS or to special libraries are lacking.

Both needs can be satisfied by using the OLE-interface (object linking and embedding) of the LabSolutions software. This interface enables access to internal functions for the use by 3rd party software. All members of Shimadzu's LabSolutions family offer such an interface, based on their modern architecture. For this reason, this type of software can be fully automated and customised for carrying out special requirements.

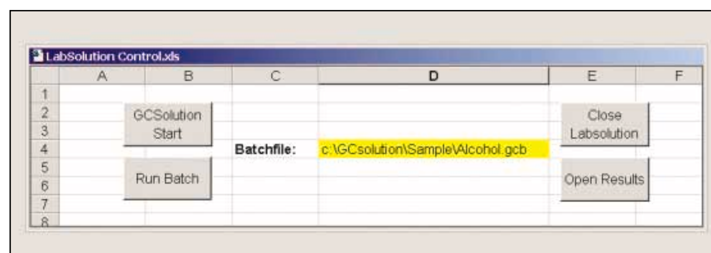


Figure 1: So simple: Setting up a user-interface with just a few menu's

In this article, we will use Excel as an automation tool in order to demonstrate the programming steps for this type of application. With its integrated VBA, Excel offers excellent possibilities to integrate and to work with external components such as the GCsolution software.

Online GC using GCsolution-OLE

The following example uses an actual project as example to show how the available functions can be used effectively for remote control of a Shimadzu GC-2010.

An online process monitoring procedure for several sample streams was setup. The analytical system consisted of a PC-controlled GC-2010 instrument with AOC-5000 autosampler and internal flow-trough cells, which were continuously circulated by the process-streams.

The problem was to automate the analytical procedure in such a way that sampling from each process-stream could take place at pre-determined time intervals, and the measured product composition as well as possible discrepancies could be passed on to a process control system.

Instrument control was taken on by a Visual Basic program, the so-called 'master'. On the one hand, the master can communicate with the GCsolution software via the OLE interface and on the other hand it can analyse the data destined for the process control system.

A prerequisite for automation is that the GC methods are defined and that pre-configured batches are used for the various measurements. For these batches, the automatic data filename creation and the automatic export of the results must be activated. The basic function of the 'master' program can be readily described in Excel:

In the VBA editor, first the 'Type Library' 'Gcanal.tlb' is integrated using the menu 'Extras/References'. In this way all available properties and methods of the component 'GCsolution' are displayed in the object catalogue <F2>. We want to use some of these methods to define a simple user-interface. The procedures described below apply to the command buttons shown in Fig. 1.

First we generate a new object of the GCsolution software, with which we will work.

```
Dim myGCSolObj As Object
Set myGCSolObj = CreateObject ("GCAppObj.Analysis")
```

Using the first procedure we open the GCsolution software and log automatically into system no. 1.

```
Sub GCSolutionStart_AtKlick()
myGCSolObj.SystemID 1
myGCSolObj.Login False, "Admin", "Password"
myGCSolObj.Show 0
End Sub
```

Subsequently, we load the batch-file selected on the worksheet and start the measurement run.

```
Sub RunBatch_AtKlick()
myGCSolObj.LoadBatchFile Range("D4").Text
myGCSolObj.startbatch
End Sub
```

After the measurement run is completed, we destroy the GCsolution object and thereby close the software. Should a batch not yet be completed, a message will appear.

```
Sub CloseLabSolution_AtKlick()
If myGCSolObj.IsBatchRun = True Then
Result = MsgBox ("Batch is running. Do you want to stop?", vbYesNo)
Select Case Result
Case vbYes
myGCSolObj.StopBatch
Case vbNo
Exit Sub
End Select
End if
Set myGCSolObj = Nothing
End Sub
```

In this way we have carried out an analysis without actually having worked directly with GCsolution.

Our Excel interface can be customised or expanded as needed. For instance via an additional button, which directly loads the exported results:

```
Sub OpenResults_AtKlick()
Workbooks.OpenText FileName:="C:\gcsolution\export\ASCII-Results.txt"
End Sub
```

The name of the exported datafile could also have been selected directly via the CloseLabSolution_AtKlick() procedure using the following commands:

```
Dim myBatchtable as GCBatchTableObj
Set myBatchtable= myGCSolObj.BatchTable
MsgBox myBatchTable.AsciiConvFileName
```

This example allows just a glimpse into the many possibilities for automation. Further applications are, for example, the retrieval of status- and error reports, the definition of batches from Excel tables or automatic Start-up/Shutdown of the GC system.

Excel lends a hand to improve reports

■ Generating reports by Excel for specialized application areas

■ How to work with macros

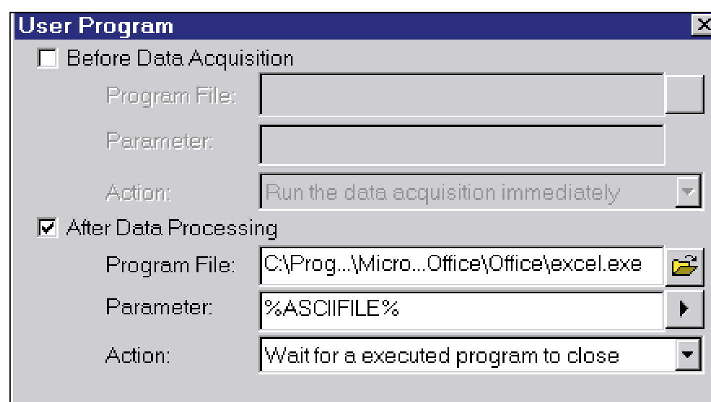
Modern chromatographic software offers various standard reports and very good report generators. With the help of Excel, reports can be generated for specialized application areas, which are not covered by standard chromatographic software.

With the easy-to-use macro recorder and the integrated Visual Basic editor, user-defined macros can be easily established. This article should be helpful for all those users who want to improve their reports with the help of Excel and are already familiar with the recording and editing of macros. All examples were generated using Excel '97.

MS Excel as "post-run" application

All chromatographic software programs from Shimadzu are capable of executing, at the end of each measurement, any external program by activating the so-called "post-run" function.

Even the measurement of the next sample can be delayed until the external program has terminated. Depending on the software version, various parameters, for example, the file name of an ASCII report can be submitted to the external program.



GCMSsolution

For example, in the GCMSsolution software, the post-run function is present as a column in the batch table; in the CLASS-VP software, the post-run function can be found under the advanced method parameters. Excel, as post-run program, automatically opens the file, which was submitted as parameter, as a new Excel worksheet. The user could now manually perform any kind of calculation or formatting or let a macro execute the same task. This macro can also print the worksheet and terminate Excel automatically.

The following examples demonstrate how different macros might look like, depending on the software version:

A file name of an ASCII file is submitted to Excel, as in the GCMSsolution software

Simultaneously to opening the ASCII file, the macro has to be loaded. To achieve the automatic loading procedure, the macro is saved with the file name "Auto_Open" as an Excel file in the directory "C:\Program files\Microsoft Office\Office\XLStart". By starting Excel, all files in this directory will automatically be opened and all macros contained in these files will be executed.

```
Sub Auto_Open() »Comment: wait 5 seconds until the calculation is started« Application.OnTime Now + TimeValue ("00:00:05"), "Manipulate_ASCII_File"
End Sub
```

The macro serves as an intermediate programme that calls the actual calculation procedure. In this case, the ASCII file will be completely loaded before using the data for calculations. The calculation procedure must be present in the same file as the "Auto_Open" procedure.

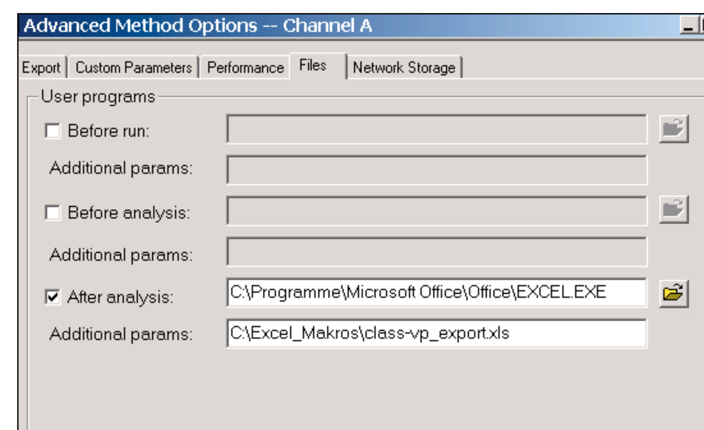

```
Sub Manipulate_ASCII_File()
If Appl.Workbooks.Count > 1 Then »Comment: only execute when opening an ASCII file (no *.xls file)«
If Right(Appl.Workbooks(2). Name, 3) < > "xls" Then »Comment: execute any calculation or formatting and close Excel«
End If
End If
Application.Quit
End Sub
```

No file name is submitted to Excel, as in the CLASS-VP 5.03 software

The name of the Excel-file containing the "Auto_Open" function is entered as a parameter into the chromatography software. In this case the Excel file may not be present in the XLStart directory. There is no need for a separate calculation procedure. The procedure for the "Auto_Open" macro can be distinguished for two different cases: In the first case, one works with a predefined ASCII file with a fixed name which will be opened by the macro:

```
Sub Auto_Open()
Workbooks.Open FileName: = "C:\Class-VP\Export\methodname-channel.area" »Comment: execute any calculation or formatting and close Exce«
Application.Quit
End Sub
```

In the second case, when the name of the ASCII file is changing, the most recent file has to be found and opened.



CLASS-VP

```
Sub Auto_Open()
With Application.FileSearch »Comment: search for the export file«
.NewSearch
.LookIn = "C:\Class-VP\Export"
.SearchSubFolders = False
.FileName = ".esd"
.MatchAllWordForms = True
.FileType = msoFileTypeAllFiles
If.Execute(SortBy:=msoSortByFileType, SortOrder:=msoSortOrderDescending) > 0 Then
If.Execute(SortBy:=msoSortByLastModified, SortOrder:=msoSortOrderDescending) > 0 Then
Workbooks.Open FileName: = .FoundFiles(1) »Comment: execute any calculation or formatting and the close Exce«
End If
End If
End With
Application.Quit
End Sub
```

The last, universal version could obviously also be used in all other cases.

However, submitting the file name directly to Excel is the safest procedure, assuming that the chromatography software offers this functionality.

Chromatography Volume 1
SOFTWARE

Automated w orkflow with MS Excel

	A	B	C	D	E	F	G
1	Sample-ID	Vial-Nr	Inj-Vol.	Methodenname	Dateiname	Sample Amount	Sample Description
2	Test1	1	100	test.met	TestDatei1	15	Nur ein Test 1
3	Test2	1	100	test.met	TestDatei2	15	Nur ein Test 2
4	Test3	1	100	test.met	TestDatei3	15	Nur ein Test 3
5	Test4	1	100	test.met	TestDatei4	15	Nur ein Test 4
6	Test5	1	100	test.met	TestDatei5	15	Nur ein Test 5
7	Test6	1	100	test.met	TestDatei6	15	Nur ein Test 6

Figure1: Excel Master Table

- **Excel helps to customise software functions**
- **Description how to utilise different software formats**

This article is to inform our readers on the possibilities to use MS Excel to enhance and customise Shimadzu's software functions.

It explains the preparation of sample tables (or "Sequence", "Batch", "Schedule") in Excel and discusses their individual formats depending on the different chromatography software packages provided by Shimadzu. All examples were prepared using Excel 97.

Excel as "Sample table" editor

All current chromatography software packages from Shimadzu are capable of importing sample tables. The sample tables have to be present as ASCII (i.e. text) files in a predefined format, which depends on the individual chromatography software package. The different formats reflect the multitude of parameters required for the various analytical methods employed.

The import of ASCII sample tables can be performed in a manner similar to opening a normal sample table in the file-menu. Preferably, the ASCII-file has the same extension used by the chromatography package in use, e.g., "seq" for CLASS-VP or "qls" for LCMSsolution.

A good example of a sample table editor is an Excel Worksheet that has one master table and, for each software package, an individual table. In the master table, all universal parameters are entered (see Figure 1).

By using formulae and, if required, macros, these entries can be copied automatically to all other tables in the worksheet. If these tables also contain suitable standard values for the instrument-specific parameters, they can simply be saved in a text format (using tab or CSV separators) and loaded into the chromatography software. Saving the worksheet can be performed using the following procedure:

```
Sub Save_ASCII()
»Comment: This procedure saves the worksheet "LCMS" as tab-separated ASCII-file«
Sheets("LCMS").Select
Sheets("LCMS").Copy
ActiveWorkbook.SaveAs _
FileName: = "C:\LCMSsolution\User\Method\ASCII_Schedule.qls",_
FileFormat: = xlText
End Sub
```

We will now illustrate the format of individual sample tables required for proper importing into the respective software package.

a) CLASS-VP

The CLASS-VP ASCII sequence has a special header and one record for each run. The separator used depends on the "list separators" of the country-specific settings of the personal computer. The detailed description of the parameters can be found in the Instruction Manual. This sequence must be saved in Excel using the CSV format. The CLASS-VP software can only import sample tables in ASCII-format, but not save them as such.

```
ASCII Batch 1
RECORD=Test,multical.met,test.dat,0,1,1,1,1,1,,,,1,,Test-Sample,1
RECORD=...
```

b) LabSolutions

The ASCII sample tables of the LabSolutions software family, e.g. GCMSsolution and GCsolution, are designed in a similar way. They are <tab> separated and consist of a header containing the column names and rows containing the values of the individual runs.

The format becomes evident if one saves an existing sample table as a text file. The ASCII file should have the extension "txt" (see Figure 2). If one opens this file in Excel using the file filter "Text documents", the structure of the text file becomes clear and can be used as a template for the sample editor worksheet.

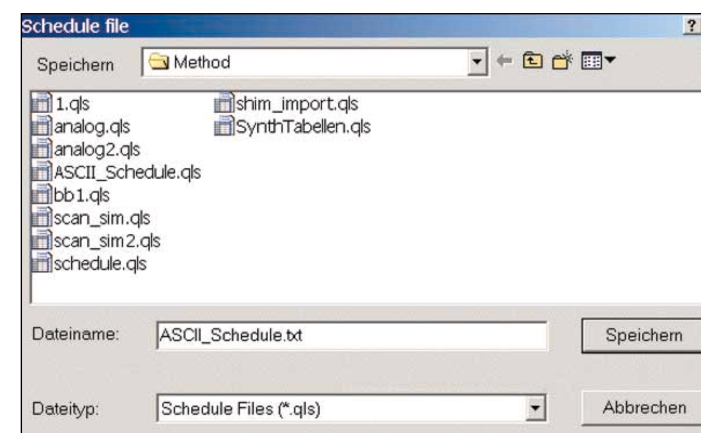


Figure 2: Save as Text

Some parameters are numerically coded; the meaning of the encoding becomes apparent if one compares the parameter table with the original sample table in the LabSolutions software. One exception is the parameter "Data Processing" in the LCMSsolution software that is encoded in a more complex way.

Figure 3 illustrates which numbers represent the various options.

These sample tables should be saved in Excel as tab-separated text format. The order and the number of columns must not be changed. Missing entries, however, will be replaced by default values in the LabSolutions software.

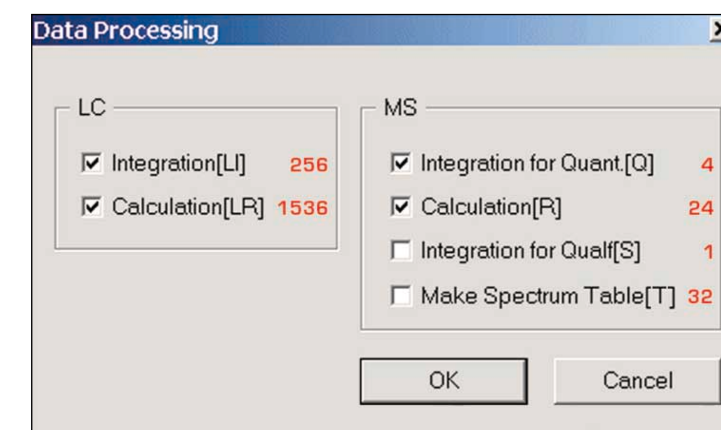


Figure 3: LCMSsolution: Parameter "Data Processing"

Don’t panic

21 CFR Part 11 and its effects on analytical data systems

- In-dept introduction into new standard
- 21 CFR Part 11 to be extended to every analytical laboratory
- Higher data and process security

The 21 CFR Part 11, or Part 11 in short for the FDA rule on electronic records and signatures, has become an often heard catch-phrase in the analytical laboratories of the pharmaceutical- and food industry in recent months. Many are wondering what to expect, what it all means and who is affected by this FDA ruling. And how Shimadzu can help in complying with these regulations.

21 CFR Part 11 – what does it mean?

The American Food and Drug Administration first released the FDA ruling on electronic records and signatures in 1997. Part 11 defines the criteria under which electronic records and electronic signatures are considered to be trustworthy, reliable, and generally equivalent to paper records and handwritten signatures. This applies to all electronic records, which are submitted to the FDA.

In addition to the security measures for the generation and release of data, a large part of the FDA ruling also applies to data archiving. As electronic records are generated by data acquisition software, most of the data management rulings deal specifically with the software itself. Although a certain software may meet all the related Part 11 requirements, FDA regulations also require that the user is sufficiently knowledgeable and trained to use the software. This is the reason why a software can support a laboratory to work FDA compliant but not solve the whole Part 11 demands by itself.

Although the FDA still accepts paper records (for example for drug registration), the aim of Part 11 is the exclusive use of electronic records instead of paper in future. This means that every drug- or food manufacturer who exports to the United States sooner or later will have to deal with electronic records and data management. Quality control in both industries are carried out using modern instrumental analytical techniques and therefore the instruments and data systems used will also have to comply with 21 CFR Part 11.

Basic requirements for analytical data systems

Part 11 defines open and closed data systems. A closed system is defined as a system that is present in an environment in which access to the system is controlled. This is usually the case in an analytical laboratory and most analytical data systems are therefore considered to be closed systems. The authenticity, integrity and, when necessary, also secure data treatment, must be ensured via control measures and protocols. Most of the regulations described in Part 11 therefore deal with the security measures against unauthorised access to the system, user management, data security, data archiving and electronic signatures.

federal register

Thursday
March 20, 1997

Part II

Department of Health and Human Services

Food and Drug Administration

21 CFR Part 11
Electronic Records; Electronic Signatures; Final Rule
Electronic Submissions; Establishment of Public Docket; Notice

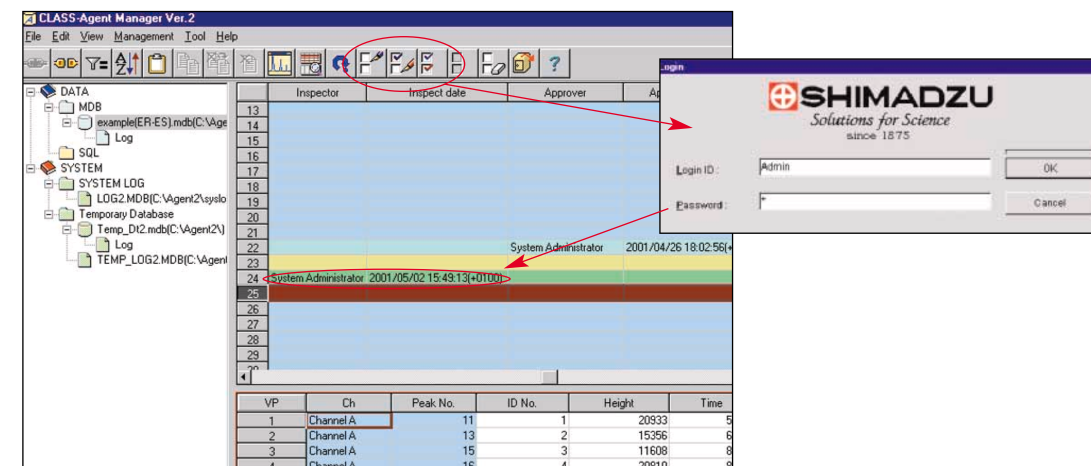
21 CFR Part 11

The following points are of special interest:

- These systems must be validated in order to ensure their accuracy, reliability, and consistant performance to meet its intended purpose
- For the purpose of inspection or auditing, it should be possible to generate copies of data in electronic as well as in human readable format during the entire required archiving period. During archiving it must be guaranteed that the data have remained unaltered
- Use of the data is limited to authorised personnel only. A Windows NT, 2000 or XP operating system is therefore recommended.
- Secure, computer generated and time-stamped audit trails must record any generation, modification or deletion of data. The audit trails must be stored along with the original electronic record and archived for the entire required period
- All users must have received proper training and must have demonstrable experience in order to use the data system
- Guidelines must be set up in order to control how users can access the system and to held them responsible for the complete data management under their user specific access code and electronic signature.

The operating system and the software often cannot completely cover all of the above requirements. If necessary so-called standard operating procedures (SOP’s) can be used to cover the missing items.

The electronic signature



Electronic signature and documentation of the audit trail

Before a data set can be supplied with an electronic signature and will be considered as a valid electronic record, the above requirements must first be met. Only then the user can apply his or her electronic signature. The electronic signature is equivalent to the handwritten signature, also with respect to any legal consequences. Therefore the signature components must be unique to a single user and must not be transferred to other persons.

The electronic signature consists, in the simplest case, of a user ID and password. Together with the signature itself, the user’s name, date and time and the meaning of the signature must be stored in the signed data set. This background information must be represented in a commonly readable format (for example as normal text). In addition, the signature must be secured from being deleted, copied or otherwise transferred to other data sets. It is easy to understand the large number of necessary control mechanisms and the importance of the signing procedures (for example the release of the final analysis results), considering the requirement of equivalence of both electronic and handwritten signature.

In addition to electronic signatures in the form of user ID and password it is possible to use biometrics to verify a signers identity for instance to recognise fingerprints. Digital signatures use cryptographic methods to unequivocally determine the identity of the user and integrity of the signed data set. Digital signatures are actually one step ahead of the present requirements of Part 11 and are therefore also recognised.

Shimadzu can help with the implementation of 21 CFR Part 11

Let’s take as example the validation, user administration, archiving and electronic signatures. System validation is carried out by trained Shimadzu personnel by implementing and documenting “Operational Qualifications” (OQ) and “Performance Qualifications” (PQ) in regular intervals. Alternatively it is possible to develop company specific validation procedures and carry them out regularly.

User administration will ensure that the access to software and data is limited to authorised personnel only. For this purpose, the normal user administration functions of the operating system can be used. Some operating systems, such as Windows 98 are not compliant with Part 11 and must be protected by numerous standard operation procedures.

The system administrator will assign certain user access rights for laboratory personnel. To get access, users must enter their user ID and a password (see above). When running the software for an extended period without any user action, the system should be able to lock the software and require the input of user ID and password to log in again.

In order to comply with the requirements relating to data protection and easy data retrieval during an audit, even years after the original analysis has been carried out, the following data must be archived: raw data (in addition to the original chromatogram or spectra also information on the sample, analytical instrumentation used and user ID), so-called meta data (such as methods, processing parameters or calibration data) and results (including compound names, concentration etc.)

When the analytical data system cannot perform these tasks completely, the easiest and most reliable way to archive data is via a database option such as the Shimadzu CLASS-Agent software. This archiving software package is based either on MS-Access, MS-SQL-server or Oracle databases and can manage data of various Shimadzu analytical systems. Chromatograms, in a generally readable format such as AIA, as well as in raw data format, together with additional information such as results, methods, sample- and user information are stored in a comprised data set. The data can be retrieved from the database, even years later, with the help of suitable search criteria.

Audit trails with time stamp will trace data and keep records on every entry into the database, all changes made to the data set as well as the actual electronic signature on the data set. Shimadzu’s CLASS-Agent software can, for example, mark different data approval steps in different colours. Electronic signatures, for example for the release of results, use User-ID and password security. The full user name, time stamp and type of operations performed will be listed in the audit trail. At present, the complete digital documentation has only rarely been brought into practice. Due to lack of suitable FDA inspections, little information is available to what level of detail the relatively general Part 11 rule should be implemented. Certainly, in many cases a plan for the implementation of Part 11 is requested by the FDA auditors during an actual inspection.

Companies that have not yet undertaken efforts to comply with Part 11, usually receive an urgent reminder. Therefore, everyone who works in a so-called regulated environment should become well-informed about these issues.

The above examples show that Shimadzu’s software developers are aware of the challenges, which they are facing in order to bring 21 CFR Part 11 compliance to every analytical laboratory.

Index

Entry	Page
21 CFR Part 11	65, 72
40 years Shimadzu GC	50
Additive analysis	62
Aldehyde analysis in printed colours	16
Allergens in parfumes	32
Animal and vegetable oils	38
AOC-5000 autosampler	52
Aroma compounds	43
Barbiturates	9
Benzodiazepine	9
BETX in water	16
Biodiesel analysis	28
Breweries	46
Chemical warfare agents	20
CLASS Agent software	65, 72
CLASS VP software	70
Clinical analysis	10
Cooled PTV	53
Constant linear velocity mode	50
Customized user interface	66
Database management	65
Dean switch	36
DI-MS (Direct Inlet)	10
DIN H53 method (GC)	14
Doping	9
Drug analysis	11
Drug screening	9
Drugs of abuse	9
Electronic record	72
Electronic signature	72
Essential oils	36
FAME analysis	28, 38
Fast-GC	38, 50, 54
Fast-GCMS	11, 18, 32, 51, 61
Food	40
GC	28, 53
GC-2010	50, 54
GC-ED	40
GC-FID	43
GC-GC system	36
GCMS	9, 16, 20, 26, 43, 46, 53
GCMS-QP2010	51
GCMSsolution software	64
GCsolution software	64, 66
GLP/GLP support	64
GLP/GMP	65
Headspace	16, 52
LabSolutions software	68, 70, 72
Large-Volume injection	22
LSD	9
MS Excel	68, 70
Multi-dimensional GC	36
NCI (Negative Chemical Ionization)	18
Oil in water analysis	14
OLE functions	66
On-column injection	14
Optic 3	53
Organochlorine pesticides	40
Organo tin compounds in textiles	26
Organophosphorous pesticides	18
Paper analysis	58
Pharmaceutical analysis	10
Polymer analysis	10, 60, 61, 62
Post-run programs	68
Productivity	11
PTV injection	22
Py-2020iD	60
Pyrolysis-GCMS	58, 60, 61, 62
Sample table	70
SPME (Solid Phase Micro Extraction)	43, 52
Sulfur compounds in CO_2	46
THC	9
TLC/MS	10
User program	46
Validation	64