Determination of Organic Acids

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- Phenolic Standards
- Acetamide Herbicide Standards

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- Optical Sensors for Alcohols and Amines

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- Water Determination in Biodiesel
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- Lewatit® Ion Exchange Resins
- Mobile Phase Additives for LC-MS

Spectroscopy
- Ultra-pure MALDI Reagents

Water Analysis
- AQUANAL® Kits
- AQUANAL® SPECTRO 3

New Product Corner
- Allergenic Dispersion Dyes Standards
- Custom Silanization of Vials
Dear Colleague,

innovación
innovazione
Innovation
inovação
innovatie

It seems that “innovation” is one of those words that can be recognized in many languages that share an alphabet. However, even beyond the word, the principle of innovation is globally-recognized as a necessary component of success; a fact that is especially true in the scientific field. Scientists face tough questions; society looks to them to solve today’s important and pressing problems: disease, clean water, clean air, the quality of food and its stable supply. Scientists need to know that their suppliers are keeping up with them, that they are just as dedicated to innovation as we are.

Sigma-Aldrich is dedicated to innovation at the basic science level, through the work of our own world-class scientists and collaboration with leading researchers in many scientific disciplines, at the product level, where we take the basic science and turn it into practical tools in the form of new and improved products, and at the service level, where we continually look for new ways of getting our products and information to you, and to make sure you can put them to immediate use to meet your specific objectives.

The key to our ability to provide practical innovative solutions is that we stay close to our customers and to the markets we serve. We visit. We listen. We ask questions. We keep abreast of new regulations and methodologies. We turn your actual requests and your unspoken needs into products. Our dedication to innovation is critical to our success, and we hope it accelerates our customers’ success as well.

Here are just a few ways we have recently provided innovative solutions to scientists:

• New innovations to HYDRANAL®, the world leader in pyridine-free Karl-Fischer titration, including new products, new patents and a new HYDRANAL® manual.
• Solid Phase Microextraction (SPME), our proprietary technology that is revolutionizing sample preparation.
• Application-specific kits, tailor-made for international test methods and new applications.
• Analytical Specialties, like ultra-pure MALDI matrix substances and new environmental standards according to EPA and other norms.
• Ionophores and auxiliary compounds for preparation of ion-selective electrodes (ISE) and optodes. We are the leading supplier of these products, and in upcoming Analytix issues we will explain the use and the advantage of our new Selectophore® ionophores.
• CHROMASOLV® solvents that meet the sensitivity demands of modern mass spectrometry.
• Our Carbon Adsorbent technology which has been used in space exploration, as well as more terrestrial applications.

There are many other innovative products I haven’t mentioned, and many more in our R&D pipeline. The articles in this issue of Analytix describe some areas of recent focus. As always, we want to hear from you. That’s how we stay current and keep the innovative products flowing.

Kind regards,

Michael Jeitziner
Feature Article

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Introduction
The measurement of organic acids in wines is complementary to sensorial and microbiological quality assessment in fermentation control, for example, because the types and concentrations of the different acids influence the resulting color and taste of the wine. Winemakers must monitor the concentration of various organic acids to ensure the quality of their wines. Tartaric, citric, and malic acid are added to adjust the pH. Malic acid levels must be monitored closely as many wines undergo a malolactic bacterial fermentation which reduces the acidity of the wine, as the malic acid is converted to lactic acid. Acetic acid is the main product of oxidation and can also spoil a wine.

In this article, we describe two different applications, both of which benefit by using high quality Fluka brand organic acid standards:

1. Determination of organic acids in red and white wines
2. Separation of organic acids in fruit juices

Part 1: Organic acids in red and white wines
Our aim in this project was to use ion exclusion chromatography for the simultaneous determination of the following organic acids of primary importance in wine: phosphoric acid, citric acid, tartaric acid, galacturonic acid, malic acid, succinic acid, lactic acid and acetic acid. Additionally, we compared two different sample preparation techniques that are common in the food industry: off-line with SPE and on-line with dialysis.

The wine samples were from Switzerland and Germany: White wine: (1) Müller-Thurgau, Baden (D), (2) RieslingxSylvaner, Graubünden (CH)
Red wine: (3) Merlot, Ticino (CH), (4) Zizerser Blauburgunder, Malans (CH)

The HPLC analyses were performed using ion exclusion chromatography with conductivity detection on a sulfonated resin in the H+ form (e.g. SUPELCOgel C-610H column or equivalent) by A. Rumi, Metrohm Ltd., Switzerland.

Sample preparation
1. Sample preparation using SPE
Wine samples spiked with organic standard solutions, non-spiked wine samples, a blank solution and standard solutions for calibration were extracted by SPE using the following protocol:

SPE protocol
- Condition the Supelclean LC-4 cartridge (Supelco, Cat. No. 57089) with 2 mL methanol followed by 4 mL eluent
- Add 1 mL sample solution with a micropipette having disposable tips
- Elute with 4 x 2 mL eluent
- Fill to the final volume with eluent

2. Sample preparation using dialysis
The wine samples and standard solutions were diluted with eluent to the final volume and dialysed (dialysis cell, Metrohm).

<table>
<thead>
<tr>
<th>Cat. No.</th>
<th>Brand</th>
<th>Description</th>
<th>Remarks</th>
<th>Package Size</th>
</tr>
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<tbody>
<tr>
<td>13669</td>
<td>Fluka</td>
<td>Acetate Ion Chromatography Standard Solution</td>
<td>1.00 g, in H₂O</td>
<td>100 mL</td>
</tr>
<tr>
<td>38730</td>
<td>Fluka</td>
<td>Citrate Ion Chromatography Standard Solution</td>
<td>1.00 g, in H₂O</td>
<td>100 mL</td>
</tr>
<tr>
<td>49897</td>
<td>Fluka</td>
<td>Formate Ion Chromatography Standard Solution</td>
<td>1.00 g, in H₂O</td>
<td>100 mL</td>
</tr>
<tr>
<td>49323</td>
<td>Fluka</td>
<td>Malonate Ion Chromatography Standard Solution</td>
<td>1.00 g, in H₂O</td>
<td>100 mL</td>
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<tr>
<td>04621</td>
<td>Fluka</td>
<td>Oxalate Ion Chromatography Standard Solution</td>
<td>1.00 g, in H₂O</td>
<td>100 mL</td>
</tr>
<tr>
<td>79409</td>
<td>Fluka</td>
<td>Phosphate Ion Chromatography Standard Solution</td>
<td>1.00 g, in H₂₃O; traceable to BAM</td>
<td>100 mL</td>
</tr>
<tr>
<td>04924</td>
<td>Fluka</td>
<td>Phthalate Ion Chromatography Standard Solution</td>
<td>1.00 g, in H₂O</td>
<td>100 mL</td>
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<tr>
<td>02717</td>
<td>Fluka</td>
<td>Propionate Ion Chromatography Standard Solution</td>
<td>1.00 g, in H₂O</td>
<td>100 mL</td>
</tr>
<tr>
<td>50824</td>
<td>Fluka</td>
<td>Tartrate Ion Chromatography Standard Solution</td>
<td>1.00 g, in H₂O</td>
<td>100 mL</td>
</tr>
<tr>
<td>57089</td>
<td>Supelco</td>
<td>Supelclean™ LC-4 SPE Tube</td>
<td>Wide pore, bed wt. 500 mg, volume 3 mL</td>
<td>54 tubes per package</td>
</tr>
<tr>
<td>59320-U</td>
<td>Supelco</td>
<td>SUPELCOGEL™ C-610H</td>
<td>30 cm x 7.8 mm ID, particle size 9 µm</td>
<td>Each</td>
</tr>
<tr>
<td>59319</td>
<td>Supelco</td>
<td>SUPELCOGEL™ H Guard Column</td>
<td>5 cm x 4.6 mm ID</td>
<td>Each</td>
</tr>
</tbody>
</table>

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determination of organic acids in various fruit beverages. This column is a cross-linked polystyrene divinylbenzene resin HPLC column prepared specifically for ion exchange analysis of organic acids. It is also ideal for separating sugars, alcohols and other fermentation products.

Analyses are best performed at low pH (a 0.1% phosphoric acid mobile phase is commonly used). Organic acids were detected in a standard mix and in grape juice cocktail at 210 nm (Figures 3 and 4). The samples were filtered through a 0.45 μm syringe-tip prior to injection onto the column.

Care should be taken in the selection of column temperature to assure the best overall separation of the components of interest. While separating a standard mix containing oxalic, citric, tartaric, malic, succinic, formic, acetic and fumaric acids at temperatures ranging from 30°C to 60°C, it was found that the retention time for fumaric acid shifted drastically. At 60°C, fumaric acid coeluted with formic acid, while it coeluted with acetic acid at 40°C. A satisfactory separation was obtained at 30°C, with fumaric acid eluting at 20 minutes. Retention time shifts for the other components were negligible.

Figure 1, Organic acid standards (after SPE)

Figure 2, Organic acids in white wine 1, Müller-Thurgau (after SPE)

Conditions (Figures 1 and 2):
Column: Ion exclusion HPLC column (H⁺ form), 25 cm x 8 mm
Mobile Phase: 1.9 mM H₂SO₄ + 2% acetonitrile in ultra pure water
Col. Temp.: 75°C; Flow Rate: 0.6 mL/min; Det.: Conductivity

Examples of the separation of an SPE extract of organic acid standards and a white wine sample are shown in Figures 1 and 2, respectively. A linear response for each acid at five different concentrations was achieved. The concentrations of the standard solutions were chosen in such a way that the whole expected concentration range of each acid in the samples was covered. The precision was determined by consecutive injections of blank wine samples and spiked ones.

Both sample preparation methods provided adequate recoveries; the SPE recoveries were 70-100%, while the dialysis gave recoveries of 82-100%. The simultaneous determination of organic acids (Table 1) with ion exclusion chromatography and conductivity detection represents a simple and fast method for the determination of this group of substances. A short analysis time is sufficient to resolve relevant acids with a concentration > 0.1g/L. The determination is fully automatable.

Part 2: Separation of organic acids in fruit beverages
This application uses a SUPELCOgel C-610H HPLC column and UV detection for the simultaneous
Optical Sensors for Alcohols and Amines

By Gerhard J. Mohr, Institute of Physical Chemistry, Friedrich-Schiller University Jena, Germany ... gerhard.mohr@uni-jena.de

Introduction

A completely new approach to the detection of electrically neutral analytes, such as alcohols, amines, aldehydes, has recently been developed that is based on reversible chemical reactions of indicator dyes with analyte molecules in polymer layers. The formation and breaking of a covalent bond between the dye and analyte causes a change in absorbance or fluorescence that can be quantified by using spectrophotometers or miniaturized optical devices. The resulting optical sensors have an operational lifetime and shelf-life that are generally superior to related enzymatic sensors for similar analytes. Possible application areas for the ethanol sensor are monitoring fermentation processes in bioreactors and measuring the ethanol content in beverages. Amine sensor layers indicate the freshness of food (e.g., histamine in fish) or detect drugs in biological fluids (e.g., amphetamines in urine). The novel dye CR-546 (Figure 1) described here is 20-fold more sensitive than its analogue ETH 4001 whose applicability for alcohol monitoring has already been evaluated in detail by the Centre for Chemical Sensors in Technopark Zurich.

Preparation of an absorbance-based sensor layer for alcohols

Dye CR-546 (1.0 mg), tridodecylmethylammonium chloride (0.2 mg), NPOE (40 mg) and PVC (80 mg) are dissolved in 0.7 mL of tetrahydrofuran. Thin layers of approximately 3-6 µm thickness are obtained by pipetting 0.2 mL of this solution on a rotating glass plate at 560 rpm using a spin-coating device. The glass plate of 3 cm diameter and 3 mm thickness serves as a mechanical support for the thin sensor layer. This layer is left to dry in ambient air for 10 minutes and is then installed in the flow-through cell.

Optical sensor for alcohol

The method can be applied to prepare a novel optical sensor to detect 1% – 15% (v/v) ethanol in aqueous solutions, with a limit of detection of 0.1% (v/v). Ethanol is evident by a color change from purple to yellow (Figure 3), which corresponds to a decrease in absorbance at 560 nm and an increase in absorbance at 480 nm (Figure 4). Response times are in the range from 15 - 30 min for both forward and reverse reactions. The layer allows for a continuous monitoring of ethanol in beverages or in bioreactors. The sensor layer is based on the chromoreactand N,N-dioctylamin-4'-trifluoroacetyl-2'-nitroazobenzene (Chromoionophore XVI), which undergoes a reversible chemical reaction with alcohols giving a simultaneous color change. The chromoreactand is incorporated into a thin layer of plasticized PVC and exposed to sample solutions containing the analyte. The calibration is performed at the same temperature as the actual measurement since the chemical reaction is affected by temperature changes.
The sensor layers are compatible with the green LED as a light source which allows the development of miniaturized devices based on CMOS (complementary metal oxide semiconductor) technology. The layers have better operational life and shelf-life than enzyme-based sensors for alcohols, with lifetimes of at least 6 months when stored in the dark at room temperature. Sensitivity for ethanol and methanol is identical, while higher sensitivity for 1-propanol is observed.

**Fluorescence-based ethanol sensor using the inner filter effect**

A fluorescent ethanol-sensitive membrane is prepared by dissolving the inert fluorophore N,N'-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide), CR-546 and the catalyst tridodecylmethylammonium chloride in the polymer matrix. The trifluoroacetate form of CR-546, with its maximum at around 560 nm, overlaps the emission of the fluorophore. Increasing ethanol concentrations decreases absorbance at 560 nm and consequently increasing luminescence of the fluorophore (Figure 5). The resulting layer has been evaluated for its detection of ethanol via changes in luminescence intensity. The calibration is linear in the range of 1% - 15% (v/v) ethanol with a limit of detection of 0.1% (v/v). Response times are in the range from 20 - 40 min for both forward and reverse reactions.

**Preparation of a fluorescence-based sensor layer for alcohol**

Dye CR-546 (1.0 mg), tridodecylmethylammonium chloride (0.2 mg), N,N'-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (S-13, 0.06 mg), NPOE (40 mg) and PVC (80 mg) are dissolved in 0.7 mL of tetrahydrofuran. A 0.2 mL aliquot of this solution is pipetted onto a rotating glass plate at 560 rpm which is then coated with a thin layer of microporous white PTFE to enhance mechanical stability and to prevent interferences from ambient light. This sensor is placed in a Jobin Yvon Spex Fluorolog 3 spectrometer and fluorescence is monitored via frontal excitation and emission detection at an angle of 22.5°.

While beer samples could be measured without any pretreatment, acidic wine samples must be adjusted to a pH above 7.0 with sodium hydroxide solution to obtain correct ethanol concentrations. Results correlated well with reported values (see Table 1). A linear calibration graph in the range of 0 – 15 % (v/v) ethanol makes two-point calibration possible.

**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reported [% (v/v)]</th>
<th>Found [% (v/v)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leikheim Premium beer</td>
<td>4.9</td>
<td>5.0 +/- 0.4</td>
</tr>
<tr>
<td>Torgauer Landbier</td>
<td>5.5</td>
<td>5.6 +/- 0.2</td>
</tr>
<tr>
<td>Blanchet white wine</td>
<td>11.0</td>
<td>11.1 +/- 0.2</td>
</tr>
<tr>
<td>Amselfelder Lieblich red wine</td>
<td>11.0</td>
<td>11.3 +/- 0.3</td>
</tr>
<tr>
<td>Blanchet Syrah red wine</td>
<td>12.5</td>
<td>11.8 +/- 0.4</td>
</tr>
</tbody>
</table>

**Absorbance-based optical amine sensor**

The chromoreactand N,N-dioctylamino-4'-trifluoroacetyl-2'-nitroazobenzene also responds to amines, provided the amines are in a gaseous form or the pH is above 10.0 to ensure the dissolved amines are non-protonated. The response to aqueous 1-propylamine, as
an example, is in the 0.5 to 50 mM concentration range with a detection limit of 0.1 mM. Amines such as triethylamine, benzylamine or amphetamine can also be detected. Response times are in the range of 2 – 10 minutes for forward and reverse reactions. Figure 6 shows the response of the sensor as a function of propylamine concentration.

**Preparation of an absorbance-based sensor layer for amine detection**

Dye CR-546 (1.0 mg), PVC (40 mg) and NPOE (80 mg) are dissolved in 0.7 mL of tetrahydrofuran. A 0.2 mL aliquot of this solution is pipetted on a rotating glass plate at 560 rpm to obtain layers of approximately 3-6 μm thickness.

**Selectivity**

The selectivity of the layers toward alcohols and amines is governed by sample pH and by the addition of a catalyst (tridecylmethylammonium chloride), which is necessary to detect alcohols. Dissolved alcohols are detected at neutral or slightly acidic pH, where amines do not interfere, while aqueous amines require a pH of above 10.0. Perm-selective microporous PTFE coatings may be attached onto the sensor layers to prevent interferences from ambient light and to enhance mechanical stability. Furthermore, they are impermeable to ions but permeable to gaseous species, e.g. amines and alcohols.

**Other applications**

The reversible chemical reaction of alcohols and amines with chromoreactand CR-546 in polymer materials may be transduced via calorimetric and capacitive microsensors, because changes in dipole moment and reaction enthalpy take place. Consequently, new and improved electronic noses can be developed because, instead of unselective polyurethanes or polysiloxanes, selective reactand-containing polymers are employed.

**References**


**Product Listing**

<table>
<thead>
<tr>
<th>Cat. No.</th>
<th>Brand</th>
<th>Description</th>
<th>Package Size</th>
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<tbody>
<tr>
<td>08709</td>
<td>Fluka</td>
<td>N,N-diocytalamino-4'-trifluoracetyl-2'-nitroazobenzene (Chromoreactand CR-546) Selectophore®</td>
<td>10 mg, 50 mg</td>
</tr>
<tr>
<td>91661</td>
<td>Fluka</td>
<td>Tridecylmethylammonium chloride Selectophore®</td>
<td>100 mg, 1 g</td>
</tr>
<tr>
<td>16459</td>
<td>Fluka</td>
<td>N,N'-bis(1-hexyloxy)perylene-3,4,9,10-bis(dicarboximide) (S-13)</td>
<td>1 mg, 10 mg</td>
</tr>
<tr>
<td>73732</td>
<td>Fluka</td>
<td>2-Nitrophenyl octyl ether (NPOE) Selectophore®, α99.0 % (GC)</td>
<td>5 mL, 25 mL, 100 mL</td>
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<tr>
<td>81392</td>
<td>Fluka</td>
<td>Poly(vinyl chloride) (PVC) Selectophore®, high molecular weight</td>
<td>1 g, 10 g, 50 g</td>
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<tr>
<td>87369</td>
<td>Fluka</td>
<td>Tetrahydrofuran (THF) Selectophore®, α99.5 % (GC)</td>
<td>10 mL, 100 mL, 500 mL</td>
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</table>

www.sigma-aldrich.com/sensorics
Phenolic Calibration Standards for Monitoring Wastewaters

By Vicki Yearick, Environmental Market Segment Manager  vyearick@sial.com

Phenolic compounds are important raw materials for the manufacture of plastic resins, pharmaceuticals, laboratory reagents, dyes, germicidal paints and general disinfectants. Because of the toxicity of many phenolics to both humans and animals, manufacturers using them or materials containing them may be required by local or regional government regulatory agencies to monitor their presence in wastewater discharges. Analysis of phenolic compounds at low levels in waste effluents can be complex, requiring extensive sample preparation followed by gas chromatography (GC). High quality analytical standards are essential for routine daily calibration of the GC instrument.

Sigma-Aldrich, through its Supelco brand, offers high quality analytical phenolic and substituted phenolic standards in the form of neat compounds, single component solutions and mixtures, all of which can be found on our web site, www.sigma-aldrich.com/standards. These standards are suitable for monitoring phenolic compounds according to United States Environmental Protection Agency (EPA), the Ontario Ministry of Environment and European Union methodologies.

Table 1 lists a sampling of Supelco brand phenolic calibration mixtures available from Sigma-Aldrich. A Certificate of Analysis is provided with each product. Multi-component solutions are certified for purity, identity and concentration. Each component is guaranteed to be within 0.5% of the stated concentration.

If you prefer a custom standard, we can also formulate, test and package phenolic calibration standards according to your specifications, saving you time and freeing your resources to focus on more pressing tasks. To obtain a quote for a custom standard, please contact our Technical Service group at techservice@sial.com, or use our new on-line Custom Standard request form available at www.sigma-aldrich.com/standards.

![Sigma-Aldrich logo]

Table 1  Phenolic compound standards from Sigma-Aldrich

<table>
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<th>Brand</th>
<th>Description</th>
<th>Pack Size</th>
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<tbody>
<tr>
<td>48859</td>
<td>Supelco</td>
<td>EPA Phenols Mix, varied concentration in methanol:  4-Chloro-3-methyl phenol (2500 μg/mL)  2-Nitrophenol (500 μg/mL)  2-Chlorophenol (500 μg/mL)  Pentachlorophenol (2500 μg/mL)</td>
<td>1 mL</td>
</tr>
<tr>
<td>2,4-Dichlorophenol (500 μg/mL)  Phenol (500 μg/mL)  2,4-Dimethylphenol (500 μg/mL)  2,4,6-Trichlorophenol (1500 μg/mL)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>47899</td>
<td>Supelco</td>
<td>EPA 8040 Phenols Calibration Mix, 500 μg/mL each in isopropanol:  2-sec-Butyl-4,6-dinitrophenol  3-Methylphenol  2,3,5,6-Tetrachlorophenol  2-Chlorophenol  4-Methylphenol  2,3,4-Trichlorophenol  2,4-Dichlorophenol  2-Nitrophenol</td>
<td>1 mL</td>
</tr>
<tr>
<td>2,3,5-Trichlorophenol  2,6-Dichlorophenol  4-Nitrophenol  2,3,6-Trichlorophenol  2,4-Dimethylphenol  Pentachlorophenol  2,4,5-Trichlorophenol  2,4-Dinitrophenol</td>
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<tr>
<td>48130-U</td>
<td>Supelco</td>
<td>MISA Group 20 Phenols Mix A, 2000 μg/mL each in methanol:  α-Cresol  2,3,4,6-Tetrachlorophenol  2,3,5,6-Tetrachlorophenol</td>
<td>1 mL</td>
</tr>
<tr>
<td>2,6-Dichlorophenol  2,3,4-Trichlorophenol  2,4-Dimethylphenol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>48131</td>
<td>Supelco</td>
<td>MISA Group 20 Phenols Mix B, 2000 μg/mL each in methanol:  p-Chloro-m-cresol  4-Nitrophenol  m-Cresol  Pentachlorophenol</td>
<td>1 mL</td>
</tr>
<tr>
<td>2-Chlorophenol  Phenol  2,4-Dichlorophenol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>861253</td>
<td>Supelco</td>
<td>Phenols Mix, 2000 μg/mL (except where noted) in 2-propanol:  4-Chloro-3-methylphenol  4-Methylphenol (1000 μg/mL)  2-Chlorophenol  2-Nitrophenol  2,4-Dichlorophenol  4-Nitrophenol</td>
<td>1 mL</td>
</tr>
<tr>
<td>2,6-Dichlorophenol  Pentachlorophenol  2,4-Dimethylphenol  Phenol  2,4-Dinitrophenol  2,3,4,6-Tetrachlorophenol</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Please visit our website: www.sigma-aldrich.com/standards to view these and our complete range of standards for nearly every analytical application.
Chloroacetanilide and Other Acetamide Herbicides for EPA Method 535 .......
Sigma-Aldrich offers twelve new standards as well as SPE tubes, solvents and HPLC columns for this LC/MS/MS method

The agriculture industry depends heavily on chemical pesticides to maintain crop quality and yield. One of the most commonly used group of herbicides in the US is the acetanilides (see Figure 1). There are six acetanilide herbicides registered in the U.S.: alachlor, acetylchlor, metolachlor, propachlor, dimethenamid and flufenacet. These compounds undergo environmental degradation to more polar, and more water soluble, ethanesulfonic acid (ESA), oxanilic acid (OA) and sulfynilacetic acid (SAA) derivatives. Because of their tendency to appear in ground and surface waters, these compounds require an analytical method for their low-level detection. The U.S. Environmental Protection Agency (EPA) Method 535 provides for the analysis of alachlor ethane sulfonic acid and other acetanilide degradation products that are listed on EPA’s 1998 Drinking Water Contaminant Candidate List.

Brief Analytical Protocol of EPA Method 535
Method 535 uses solid phase extraction with a nonporous graphitized carbon sorbent to extract the ethane sulfonic acid (ESA) and oxanilic acid (OA) acetanilide herbicide degradates from finished drinking water matrices. The power of HPLC coupled with tandem mass spectrometry (LC/MS/MS) is harnessed to separate and quantify these highly polar and closely-related analytes. Dimethachlor-ESA and butachlor-ESA are the suggested surrogate and internal standard, respectively.

Solid Phase Extraction
Analytes and surrogates are extracted and concentrated by passing the water sample through a solid phase extraction (SPE) cartridge containing a nonporous graphitized carbon (e.g. Supelclean™ ENVI-Carb™; Supelco Cat. No. 57094). The compounds are eluted with a small quantity of methanol containing 10 mM ammonium acetate. The methanol extract is then concentrated to dryness and reconstituted in a small volume of 5 mM ammonium acetate.

LC/MS/MS
LC/MS/MS is an ideal tool for the analysis of acetanilide derivatives because it provides both the specificity and sensitivity required to identify and quantify them in often complex environmental samples. An ion trap instrument was employed during method development and is preferred because it is rugged, reliable and provides quantitative results. The EPA method recommends separation on a reversed phase (C18) column (e.g. Ascentis™ C18). HPLC columns and mobile phase solvents must be chosen to give the negligible background that facilitates low-level detection.

The heart of the analysis: Reliable acetanilide standards
The concentration of each component is measured by an internal standard procedure, that is, by relating the product ion response of that compound to the product ion response of the compound that is used as an internal standard. A surrogate analyte, whose concentration is known in every sample, is measured with the same internal standard calibration procedure.

 Sigma-Aldrich has responded to frequent customer requests by introducing 12 unique pesticide metabolites which are listed in EPA 535. In addition to these standards, we also offer all sample preparation products, solvents and HPLC columns that meet the requirements of this sensitive LC/MS/MS method.

By Rainer Walz, Product Manager Analytical ... rwalz@sial.com

Sample Preparation and Analysis Products
The Sigma-Aldrich family includes Supelco-brand chromatographic and sample prep products and Riedel-de Haën-brand solvents that are ideal for EPA 535 and other LC/MS/MS applications. For Solid Phase Extraction the Supelclean ENVI-Carb™ cartridges (0.5 g/tube, 6 ml; Supelco Cat. No. 57094) are particularly suited. The chromatographic and LC/MS/MS analyses can be done conveniently by employing an Ascentis™ C18 column (5 cm x 2.1 mm ID; 5 μm particles; Supelco Cat. No. S81303-U). For the mobile phase we highly recommend our high-purity family of CHROMASOLV® solvents and solvent blends. A complete list can be found on the internet under www.sigma-aldrich.com/chromasolv.

www.sigma-aldrich.com/standards
Measure Water Content in Biodiesel Fuels ........ Efficient, reliable and rapid moisture determination using HYDRANAL® reagents

By Helga Hoffmann, Technical Support HYDRANAL® Manager ... hhoffman@europe.sial.com
and Michael Jeitziner, Market Segment Manager Analytical Reagents ... mjeitziner@sial.com

Water content in biodiesel can be determined reliably and reproducibly with Karl Fischer titration using HYDRANAL® reagents (2), as described in this article.

Volumetric Titration
In general, we use HYDRANAL® Composite 2 as a titration agent. Ethanol-based, non-toxic HYDRANAL® CompoSolver E (30 mL) is placed in the titration vessel and titrated to dryness with HYDRANAL® Composite 2. The biodiesel sample (5 mL), precisely measured using differential weighing, is injected into the titration vessel and titrated.

HYDRANAL® CompoSolver E can be replaced with HYDRANAL® LipoSolver CM, which contains chloroform as a solubilizing agent, or HYDRANAL® LipoSolver MH, which contains 1-hexanol, or HYDRANAL® Methanol Rapid.

Coulometric Titration
DIN EN 14214/ISO 12937 states that water determination in biodiesel should be carried out by coulometric KF titration method. The coulometric procedure is significantly more sensitive than the volumetric titration. Biodiesel components contain double bonds that can react with iodine, leading to erroneously high results. We observed a small tendency toward this side reaction, but not enough to interfere with the analysis. Falsely high results are evident by extremely fading end points, a typical sign of the side reaction.

We also tested various reagents in cells with and without a diaphragm for coulometric determination of water content. A volume of 5 mL of biodiesel was selected as a single injection in each case, always weighed using the differential weighing method. The precision of the sample manipulation and the coulometric cell can be tested by means of HYDRANAL® Water Standard 0.10.

Procedure: Coulometry with diaphragm
HYDRANAL® Coulomat CG (5 mL) is placed in the cathode chamber of a coulometric cell and approximately 100 mL HYDRANAL® Coulomat Oil is placed in the anode chamber up to the same level. The coulometer is switched on, and the cell is automatically titrated to dryness. When the drift stabilized at < 10 µg/min, a 5 mL sample that has been precisely measured using differential weighing is injected.

www.sigma-aldrich.com/hydranal
Procedure: Coulometry without diaphragm
This titration follows the same procedure as for coulometry with a diaphragm, except HYDRANAL® Coulomat AG-H replaces HYDRANAL® Coulomat CG.

Determining the water content using the Karl Fischer oven
Using a KF oven, the biodiesel sample was gradually heated from 50°C to 250°C to test the characteristics of the sample. The temperature ramp indicated that the water was already released by the time the oven reached 80°C. At approximately 120°C, a slight side reaction occurs. At approximately 190°C the sample emits smoke and decomposes. The temperature profile suggested that 100°C is suitable for evaporation of the biodiesel sample.

Determining the water content using the Karl Fischer oven
HYDRANAL® Coulomat CG (5 mL) is placed in the cathode chamber of a coulometric cell with diaphragm and approximately 100 mL HYDRANAL® Coulomat AG Oven is placed in the anode chamber up to the same level. A 4 mL biodiesel sample, evaporated as previously described above, is titrated in this manner.

The cell without a diaphragm requires only 100 mL HYDRANAL® Coulomat AG Oven. HYDRANAL® Molecular Sieve 0.3 nm is well suited as a drying medium for the carrier gas. HYDRANAL® Coulomat AG Oven can also be replaced with HYDRANAL® Coulomat AG or HYDRANAL® Coulomat AD.

References
[2] Laboratory Application L 546*

* Laboratory Applications
Please contact our HYDRANAL® Laboratories (hhoffman@europe.sial.com). We will be glad to send you our Laboratory Reports by fax or e-mail. You can also find the full list on our website www.sigmaaldrich.com/hydranal.

Product Listing

<table>
<thead>
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<th>Brand</th>
<th>Product</th>
<th>Used as…</th>
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<tbody>
<tr>
<td>34806</td>
<td>Riedel-de Haën</td>
<td>HYDRANAL® Composite 2</td>
<td>One component reagent, titre: 1 mL – 2 mg water</td>
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<tr>
<td>37855</td>
<td>Riedel-de Haën</td>
<td>HYDRANAL® LipoSolver CM</td>
<td>To use with HYDRANAL® Composite for titration of non-polar substances, fats and oils</td>
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<tr>
<td>37856</td>
<td>Riedel-de Haën</td>
<td>HYDRANAL® LipoSolver MH</td>
<td>To use with HYDRANAL® Composite for titration of non-polar substances, fats and oils</td>
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<tr>
<td>34734</td>
<td>Riedel-de Haën</td>
<td>HYDRANAL® CompoSolver E</td>
<td>Methanol-free working medium</td>
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<tr>
<td>37817</td>
<td>Riedel-de Haën</td>
<td>HYDRANAL® Methanol Rapid</td>
<td>Solvent for a fast Karl-Fischer titration, max. 0.02% water</td>
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<td>34807</td>
<td>Riedel-de Haën</td>
<td>HYDRANAL® Coulomat A</td>
<td>Anolyte for cells with diaphragm, reagent contains chloroform</td>
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<tr>
<td>34868</td>
<td>Riedel-de Haën</td>
<td>HYDRANAL® Coulomat Oil</td>
<td>Anolyte for titration of oils</td>
</tr>
<tr>
<td>34843</td>
<td>Riedel-de Haën</td>
<td>HYDRANAL® Coulomat AG-H</td>
<td>Anolyte for titration of long-chained hydrocarbons free of halogenated hydrocarbons</td>
</tr>
<tr>
<td>34739</td>
<td>Riedel-de Haën</td>
<td>HYDRANAL® Coulomat AG Ov en</td>
<td>Anolyte for determination with KF-oven</td>
</tr>
<tr>
<td>34840</td>
<td>Riedel-de Haën</td>
<td>HYDRANAL® Coulomat CG</td>
<td>Cathode, free of halogenated hydrocarbons, 25 mL bottle resp. 10 x 5 mL ampoules</td>
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<tr>
<td>34847</td>
<td>Riedel-de Haën</td>
<td>HYDRANAL® Water Standard 0.10</td>
<td>1 g contains 0.10 mg = 0.01 % water, contains 10 glass ampoules of 4 mL, traceable to NIST SRM 2890</td>
</tr>
<tr>
<td>34241</td>
<td>Riedel-de Haën</td>
<td>HYDRANAL® Molecular sieve 0.3 nm</td>
<td>Drying agent for Karl Fischer applications</td>
</tr>
</tbody>
</table>

Technical Support
If you have further questions concerning HYDRANAL®, its use and applications, please contact us at:

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Fax +49-5137/8238-698
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HYDRANAL® Technical Center
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Tel. +1-800- HYDRANAL® (toll-free hotline for USA and Canada)
Fax +1-314-771-5765
e-mail: dclark@sial.com

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HYDRANAL® Manual
Updated for 2006

• HYDRANAL® is the gold standard reagent line for pyridine-free moisture determination by Karl-Fischer titration.

• The HYDRANAL® Manual is your one-stop reference for everything you need to know about HYDRANAL®

As always, the HYDRANAL® Manual laboratory handbook provides practical, up-to-date information on Karl-Fischer titration including:
• Principles of Karl Fischer titration
• Standard procedures for volumetric and coulometric titration
• Selection of the appropriate solvents for the sample
• Sample handling techniques
• Complete HYDRANAL® product listing

This year, we've updated the HYDRANAL® Manual with:
• New! HYDRANAL® products, like HYDRANAL® Medium K, a safer solvent for the analysis of Aldehydes and Ketones and HYDRANAL® Solver (Crude) Oil, a solvent for the analysis of Crude Oil samples
• New! HYDRANAL® Applications
• New! HYDRANAL® Lab Reports
• New! HYDRANAL® Literature

Please call or visit our website to obtain your personal copy of our HYDRANAL® Manual.

www.sigma-aldrich.com/hyranal_manual
Lewatit® Ion Exchange Resins – All-around Solutions for Chemical Processes

Time- and application-tested products with a high potential for innovation

By Stefan Neumann, Ion Exchange Resin Business Unit, LANXESS Deutschland GmbH Leverkusen

The following actual examples from a range of industries provide impressive illustrations of the resins’ wide applicability. Most of these processes have already been implemented on an industrial scale, although some are still at the pilot stage:

Purification of organic liquids: As well as demineralizing and deacidifying organic solvents such as alcohols, ketones, polyethers, petrochemical C4-C5 fractions and natural gas condensates, organic components can also be removed from organic liquids by means of special binding mechanisms. For example, one forward-looking application for Lewatit® is the removal of glycerin from biodiesel or the recovery of noble metal catalysts.

Catalysis of organic reactions: As immobilized acids, ion exchange resins catalyze the synthesis of bisphenol A, MTBE, TAME, phenol alkylates and esters, for instance. Furthermore, they can also support the splitting of disaccharides or esters, such as methyl acetate.

Purification of chemicals: Various types of impurities can be removed from concentrated brines (NaCl, NaNO3, KCl, MgCl2), sodium hydroxide solution, hydrazine, ammonia, chromate solution and hydrogen peroxide, among others, and also from organic liquids such as alcohols, biodiesel or C4-C5 fractions. Ion exchange resins can thus have a positive effect on the lifetime and quality of a wide range of electrolyte solutions, such as those used in electroplating.

Acid recovery: Even highly dissociated acids with concentrations of up to 30 percent can be freed of impurities (such as metal ions) using Lewatit®, thus enabling cycles of consistent quality in etching baths.

Metal recovery: The enrichment, isolation and pure-state preparation of a wide range of metals is possible on scales both large (e.g. mines) and small (e.g. secondary flows in chemical processes). The selectivity of ion exchange resins is exploited to enrich and concentrate specific metal ions from process streams.

Wastewater treatment: Selective exchange resins enable the removal of heavy metals from wastewater streams. Alkali metals and alkaline earth metals, which are much less problematic in environmental terms, are

Chemical processes comprise the steps of processing chemical starting materials, synthesizing the products, isolating the generated materials from the reaction mixture and subsequent purification. In the broader context of industrial processes, the steps also include detoxifying waste streams to protect the environment and recovering valuable materials. The ion exchange resins from the extensive Lewatit® product range from LANXESS Deutschland GmbH have been put to use successfully in all of these important steps.

Researchers and production and application technicians of the LANXESS Ion Exchange Resins business unit have tailored the ion exchange resins’ characteristics as catalysts or selective adsorbents for demanding and, in some cases, exotic reaction conditions to meet our customers’ specific requirements. Ion exchange resins have been designed and modified for customized process solutions. Their use today extends far beyond that of softening or demineralizing water and has moved profitably into new and demanding areas of application.

Several dozen different processes have been used successfully for years. New product development is constantly driven forward by the diverse range of products and processes available, increasingly strict environmental requirements, rising raw material prices and an increasing scarcity of resources. Ion exchange resins offer a high potential for innovation in a range of applications. They enable processes involving complex chemistry to be configured with relatively simple apparatus.

Figure 1
Thorough quality check of Lewatit® ion exchangers in a modern production site in Bitterfeld, Germany
not affected and remain in the water. Threshold values with residual concentrations in the ppb range can be maintained in situations where simple precipitation methods generally fail. Alongside the separation of heavy metals, ion exchange resins and adsorber resins can also be used for the selective removal of boron, ammonia, cyanide, fluoride and a range of organic compounds.

**Groundwater purification:** Groundwater contaminants such as cyanide, chromate, nitrate, heavy metals, arsenic, organic impurities, ammonia and fluoride can be removed using Lewatit®.

**Waste air purification:** Acidic ion exchange resins adsorb alkali gases such as NH₃, while alkali ion exchange resins adsorb acidic gases, such as HCl and SO₂. Systems for purifying small gas streams are already in use in clean rooms.

**Soil purification:** Lewatit® can be used to bind and immobilize heavy metal contaminants in the soil. This prevents toxic substances from being leached into the groundwater or taken up by plants.

**A modular system for customized ion exchange solutions**

The selectivity of the functional groups integrated into the resin beads is generally the key to how the application functions. The appropriate chemical group must be selected from some twelve possible options. Furthermore, loading the resin with metal ions such as palladium, iron, zinc, calcium and aluminum represents further ways of controlling the reaction and binding possibilities in the resin.

The efficiency of the process can also be controlled via the inner (pore structure) and outer resin structure (particle size distribution). Thus, the introduction of ion exchange resins with a narrower particle size distribution, known as monodisperse resins, was a key milestone in product optimization. New production techniques and corresponding improvement of both the outer and inner structure of the resin beads enabled improved exchange reaction kinetics and osmotic stability of the material. Success was achieved via higher usable capacities, a higher selectivity in separation processes and also a longer resin life expectancy.

While the first generation of monodisperse resins generally had bead diameters of 0.5-0.6 mm, further developments are aimed at producing specific monodisperse grades with larger or smaller particle sizes. Smaller beads are particularly attractive for processes in which fast kinetics, high usable capacities and sharply defined reaction zones are necessary. Coarser grains are particularly interesting for hydro-metallurgical applications, where technical requirements related to pressure drop are preeminent. Further, a controlling effect on the selectivity of reactions can be achieved via the degree of substitution and cross-linking on the polymer structure.

With over 100 products, LANXESS offers a range of ion exchange resins that can be used as a modular system to create individually tailored solutions. Collaboration is an attractive option for customers because it offers both the range of high quality products and the ability to work one-on-one with our expert chemists and process technicians in the applications laboratory.

<table>
<thead>
<tr>
<th>Cat. No.</th>
<th>Description</th>
<th>Remarks</th>
<th>Application</th>
</tr>
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<tbody>
<tr>
<td>62103</td>
<td>Lewatit® MonoPlus TP-207</td>
<td>Weakly acidic, macroporous cation exchange resin with chelating imino-diacetate groups</td>
<td>Selective binding of heavy metal ions from weakly acidic to weakly basic solutions</td>
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<td>62108</td>
<td>Lewatit® MonoPlus TP-260</td>
<td>Weakly acidic, macroporous cation exchange resin with chelating aminomethyl phosphonic acid groups</td>
<td>(1) Refined purification of alkali chloride brines; (2) extraction/recycling of heavy metal ions</td>
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<tr>
<td>62105</td>
<td>Lewatit® MonoPlus TP-208</td>
<td>Weakly acidic, macroporous cation exchange resin with chelating imino-diacetate groups</td>
<td>Selective binding of alkaline earth ions and heavy metal ions</td>
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<tr>
<td>62107</td>
<td>Lewatit® MonoPlus TP-214</td>
<td>Monosperical, macroporous chelating resin with thiourea groups</td>
<td>Removal of Hg/Ag/Au/Pt from aqueous solutions</td>
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<tr>
<td>62084</td>
<td>Lewatit® MonoPlus K-2629</td>
<td>Strongly acidic macroporous polymer-based resin in spherical bead-form with sulfonic acid groups</td>
<td>(1) heterogeneous catalyst for organic reactions (e.g. esterification, etherification) (2) processing of aqueous and organic liquids</td>
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<tr>
<td>17293</td>
<td>Lewatit® VP OC-1131</td>
<td>Cation exchange resin crosslinked polystyrene matrix with adsorbed di-2-ethylhexylphosphate</td>
<td>Removal of heavy metal ions from acidic and neutral solutions</td>
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</table>
Mobile Phase Additives for LC-MS. Part 2: How to Overcome Suppression Effects of TFA ....... This is the second installment in a five-part series on mobile phase additives for LC-MS to appear in each of the issues of Analytix in 2006.

By Joachim Emmert, Senior Scientist R&D Fluka / Riedel-de Haën ... jemmert@sial.com
and Alex Rueck, Scientist R&D Fluka / Riedel-de Haën ... arueck@sial.com

Mobile phases for HPLC of proteins and peptides usually contain trifluoroacetic acid (TFA) to control the pH and improve peak shape and resolution. TFA enhances retention by ion pairing with the peptide and improves peak shape by reducing silanol interactions (1). However, TFA has adverse effects on MS detection. Its high surface tension prevents efficient spray formation and TFA ions in the gas phase ion-pair with the peptide's basic groups suppressing their ionization and reducing the MS signal (2, 3, 4). When TFA cannot be avoided, its effects can be mitigated by additional use of other acids, like formic or propionic acid, either post-column or as so called triple blends (Tables 1 and 2).

All analytical conditions and test compounds were the same as already described in the first article (5), using TFA as additive instead or the triple blends as solvents respectively. Propionic acid was added post column / pre electrospray via T-piece as a 10% solution in 2-propanol. For additional experiments, a peptide mixture (pepmix) was prepared to study the specific influence on this kind of separation. The test compounds and the pepmix were both separated on a Supelco Discovery HS C18 column, 15 cm x 2.1 mm ID, 5 μm particle size; the 5 components (peptides) of the pepmix are listed in Table 3. MS-EIC traces are the same for all chromatograms.

Figure 1 shows the separation without any additive. Under these conditions, the basic peptide bradykinin is barely distinguishable from the baseline. Its mass spectrum can still be obtained (Figure 2, lower), showing the doubly-charged molecular ion [M+2H]²⁺ with m/z = 1061.6 or m/z = 530.8. Raffinose is unaffected by adding TFA or other organic acids. Its spectrum (Figure 2, upper) shows the H⁺ (505 m/z) and NH₄⁺ addsucts (522.1 m/z) and the high abundance Na⁺ adduct (527.1 m/z).

Addition of 0.1% TFA (Figure 3, top) causes all five test compounds to elute as well separated and sharp peaks. However, note that sensitivity drops almost 10-fold. The suppression effect is reduced by using 0.1% TFA and adding propionic acid (10% in 2-propanol) post-column (Figure 3, middle), an effect described in detail by Apfel et al. (2). Using the triple-blend of 0.1% formic acid/0.01% TFA (Figure 3, lower) greatly improves the signal, but with a compromise. Compared to TFA alone, resolution is poorer; and compared to formic acid alone (5), sensitivity is poorer.

The three additives can be used in synergy, by balancing their benefits and limitations. Add small amounts of TFA to formic or propionic acid to improve peak shape;
reduce TFA and add formic or propionic acid to improve the MS signal. Other MS and chromatographic parameters also influence this decision, including analytes, column packing material and dimensions, length of mixing zone, flow rate, etc. (1, 2). This is especially true for peptide separations. The charge state of the molecular ion is not affected by this and varies in the pepmix between singly-charged (bradykinin fragment 1-7) and triply-charged (insulin oxidized B chain) (Table 3). Depending on instrument and conditions it may be the case that one peptide appears in more than one charge state, i.e. doubly- and triply-charged in one spectrum (Figure 4).

In summary, the ionization-suppressing effects of TFA can be partly overcome by addition of other LC-MS compatible organic acids, like formic or propionic acid. For convenience and to guarantee reliable composition, Sigma-Aldrich offers pre-blended LC-MS mobile phases that contain acidic additives in high purity LC-MS CHROMASOLV® grade solvents. Our triple blends contain TFA with formic acid to provide both MS sensitivity and chromatographic performance.

References
Ultra-pure MALDI Reagents .......... The quality that meets your highest demands

Introduction
MALDI (matrix-assisted laser desorption/ionization) expands the application of mass spectrometry toward the analysis of high molecular weight, non-volatile and thermally labile compounds, such as intact proteins and oligonucleotides. It also requires relatively little sample preparation and is more amenable to topological imaging compared to other forms of MS ionization.

In MALDI, the sample is mixed with a chemical matrix that absorbs incident laser light energy, vaporizing the spot under the incident laser and producing intact gas-phase ions. Although there have been numerous experiments to simplify MALDI by eliminating the sample-matrix mixing step, like direct MS from solid supports or 2D-gels, using a matrix substance (chemical) is still the most common approach.

Quality of MALDI matrices
A typical MALDI matrix substance is an aromatic acid with a chromophore that absorbs strongly at the wavelength of the incident laser. The importance of the matrix substance cannot be overstated; the success of a MALDI experiment depends on the right choice of matrix and its quality. Organic impurities can lead to extraneous peaks, especially in the low mass range. Trace levels of ions, especially Na⁺ and K⁺, form adducts with sample molecules. These adducts differ in mass according to the number of positive ions and complicate the MS spectrum. Because of the strict purity requirements for both organic impurities and inorganic ions, many MALDI users have been forced to purify commercially available, but impure, matrix substances.

New, Fluka-brand high purity MALDI matrix substances
Due to the success of our range of MALDI matrices, the ever-increasing sensitivity of MALDI instruments and an ongoing trend to decreasing sample quantities (e.g. from excised spots from 2D-gels in proteomics) we recently figured out a process for the manufacture of MALDI matrix substances with even higher purity, superior to anything that was technically feasible previously.

Our first offering in the new, ultra-pure line includes the three most common matrix substances, α-cyano-4-hydroxycinnamic acid (HCCA), 2,5-dihydroxybenzoic acid (gentisic acid) and sinapic acid (Table 1). The strict, application-based specifications for the new, ultra-pure MALDI matrix substances include:

- Purity > 99.5%
- Large set of trace impurity specifications, typically below 1 mg/kg (< 1 ppm)
- Appearance and solubility requirements

Fluka MALDI substances are extensively purified to meet these specifications and provide sufficient quality to meet the most demanding applications.

Excellent solubility and performance
One of the most important aspects of the new ultra-pure MALDI substances from Fluka is their ability to dissolve rapidly and completely; a brief vortex mixing is typically sufficient. Actual performance of the new ultra-pure MALDI substances in situ is demonstrated in the accompanying figures with a test mixture of five peptide standards from Sigma’s ProteoMass™ line (Table 1). MALDI experiments were performed on a Kratos PC Axima CFR V2.4.1 in Reflectron mode.

The comparison of MALDI mass spectra using the ultra-pure grade HCCA versus standard grade is shown in

Table 1 ........ MALDI Products from Sigma-Aldrich

<table>
<thead>
<tr>
<th>Cat. No.</th>
<th>Brand</th>
<th>Product</th>
<th>Package Size</th>
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<tr>
<td>39468</td>
<td>Fluka</td>
<td>α-Cyano-4-hydroxycinnamic acid (HCCA) puriss. p.a., &gt;99.5% (HPLC)</td>
<td>10 x 10 mg</td>
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<td>39319</td>
<td>Fluka</td>
<td>2,5-Dihydroxybenzoic acid (Gentisic acid) puriss. p.a., &gt;99.5% (HPLC)</td>
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<tr>
<td>49508</td>
<td>Fluka</td>
<td>Sinapic acid puriss. p.a.</td>
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ProteoMass™ MALDI-MS Peptide Standards

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<td>P2613</td>
<td>Sigma</td>
<td>ProteoMass™ P14R MALDI-MS Standard</td>
<td>5 x 10 nmol</td>
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<td>B4181</td>
<td>Sigma</td>
<td>ProteoMass™ Bradykinin Fragment 1-7</td>
<td>5 x 10 nmol</td>
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<tr>
<td>A8846</td>
<td>Sigma</td>
<td>ProteoMass™ Angiotensin II</td>
<td>5 x 10 nmol</td>
</tr>
<tr>
<td>A8346</td>
<td>Sigma</td>
<td>ProteoMass™ ACTH Fragment 18-39</td>
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<tr>
<td>I6154</td>
<td>Sigma</td>
<td>ProteoMass™ Insulin chain B oxidized</td>
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LUCY™ Fluorescent Dyes (5 mg/mL in DMSO, 5000 X Stock solution)

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<td>43772</td>
<td>Fluka</td>
<td>LUCY- 565</td>
<td>500 µL</td>
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<tr>
<td>41629</td>
<td>Fluka</td>
<td>LUCY- 569</td>
<td>500 µL</td>
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</table>

www.sigma-aldrich.com/maldi_matrices
**Figure 1**
Comparison of MALDI-MS spectra provided by ultra-pure and regular grade HCCA

![HCCA Ultra-pure grade (Cat. No. 39468)](image1)

**Figure 1a**
HCCA Ultra-pure grade (Cat. No. 39468)

**Figure 1b**
HCCA regular grade

Sample: 0.7 μL ProteoMass™ peptide mix (bradykinin (1.5 μM), angiotensin II (1.0 μM), P14R (0.5 μM), ACTH (1.0 μM), insulin B-chain (2.0 μM), mixed with 0.7 μL HCCA matrix in AcN/0.1% TFA MALDI-MS: Kratos PC Axima, reflectron mode, laser power 85%.

**Figure 2**
Comparison of MALDI-MS spectra provided by ultra-pure and regular grade HCCA: 10-fold diluted sample

![HCCA Ultra-pure grade (Cat. No. 39468)](image2)

**Figure 2a**
HCCA Ultra-pure grade (Cat. No. 39468)

**Figure 2b**
HCCA regular grade

Sample: 0.7 μL ProteoMass™ peptide mix (bradykinin (150 nM), angiotensin II (100 nM), P14R (50 nM), ACTH (100 nM), insulin B-chain (200 nM), mixed with 0.7 μL HCCA matrix in AcN/0.1% TFA MALDI-MS: Kratos PC Axima, reflectron mode, laser power 85%.

**Figure 3**
Ultra-pure HCCA MALDI-MS spectrum of β-Galactosidase digest, excised 1D-gel band following LUCY-506 staining

**Conclusion**
Recently introduced, ultra-pure matrix substances, including HCCA, 2,5-dihydroxybenzoic acid (gentisic acid) and sinapic acid, contain vanishingly low levels of both organic impurities and inorganic ions. LUCY fluorescent dyes improve visualization of peptides in 1D- and 2D-gels compared to competitive dyes. The ProteoMass line of peptide standards is ideal for troubleshooting and calibrating sensitive MALDI-MS instruments.

For a complete listing of our MALDI matrix substances and related calibration products please visit our web site: [www.sigma-aldrich.com/maldi_matrices](http://www.sigma-aldrich.com/maldi_matrices)
Complete Solutions for Mobile Water Analysis ...... AQUANAL® Compact Labs contain everything needed for mobile, quick and easy on-the-spot water analysis

By Klaus Buckendahl, European Sales Development Manager, and Michael Jeitziner, Market Segment Manager Analytical Reagents ... aquanal@sial.com

Sigma-Aldrich's AQUANAL® Compact Labs are kits that provide mobile professional water tests with on-the-spot results for various types of processed waters (drinking, aquarium, pool, waste, spring, mineral, etc.), natural surface waters (lakes, ponds, rivers, etc.) and water from industrial processes. AQUANAL® Compact Labs provide users with rapid results whether detection is by colorimetry (by comparing color change using color charts), titration or photometry*. They contain all tests and reagents needed for a particular field of work. Typical applications for the compact labs are:

**General water quality measurements** – for monitoring various water parameters

**Fish culture water** – for fish farms and fish tank owners to measure important water quality parameters important to the health of the fish stock

**Ökotest** – for measurement of ecologically relevant parameters in surface waters, like ponds, lakes and streams

**Education** – for schools, training labs and in-class teaching on titration and other water testing techniques

**Emergencies** – for on-the-spot measurements by first responders like fire brigades, environmental protection officers and local authorities

Table ......... Parameters determined by the various AQUANAL® Compact Labs

<table>
<thead>
<tr>
<th>Lab Type</th>
<th>Compact Lab*</th>
<th>EduCase</th>
<th>Ökotest Water Lab</th>
<th>Ökotest Water Lab Low Phosphate</th>
<th>Fishwater Lab</th>
<th>Analytical Case for Building Restoration*</th>
<th>Pool tester</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat. No.</td>
<td>37562</td>
<td>37518</td>
<td>37557</td>
<td>37543</td>
<td>37566</td>
<td>37563</td>
<td>37546</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0.2 - 8.0 mg/L</td>
<td>≤ 0.05 - 10 mg/L</td>
<td>≤ 0.05 - 10 mg/L</td>
<td>≤ 0.05 - 10 mg/L</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td>0.1 mL = 14.2 mg/L Ca</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonate Hardness</td>
<td>0.1 mL = 2°C CH</td>
<td>1 drop = 1°C CH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloride</td>
<td>5 – 300 mg/L</td>
<td>0.1 mL = 20 mg/L Cl</td>
<td>2 - 100 mg/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.01 - 0.3 mg/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td>0.005 - 0.1 mg/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>0.05 - 4.5 mg/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Cyanide (total)</td>
<td>0.03 - 0.7 mg/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Iron</td>
<td>0.2 - 15 mg/L</td>
<td>&lt; 0.05 - 1.0 mg/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Magnesium</td>
<td>0.02 - 0.5 mg/L</td>
<td>100 - 1,500 mg/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>0.02 - 0.5 mg/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrate</td>
<td>1 - 50 mg/L</td>
<td>10 - 80 mg/L</td>
<td>0.5 - 50 mg/L</td>
<td>10 - 80 mg/L</td>
<td>0.5 - 50 mg/L</td>
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<td></td>
</tr>
<tr>
<td>Nitrite</td>
<td>0.005 - 0.1 mg/L</td>
<td>0.02 - 1.0 mg/L</td>
<td>0.02 - 1.0 mg/L</td>
<td>≤ 0.02 - 1.0 mg/L</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>0.1 - 3.0 mg/L</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Phosphate</td>
<td>0.02 - 0.4 mg/L</td>
<td>0.5 ≤ 6.0 mg/L</td>
<td>0.02 - 0.4 mg/L</td>
<td>0.5 ≤ 6.0 mg/L</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total hardness</td>
<td>1 drop = 1°dH</td>
<td>0.1 mL = 20 mg/L CaO = 2° dH</td>
<td>1 drop = 7.19 mg/L Ca = 1°dH</td>
<td>1 drop = 7.19 mg/L Ca = 1°dH</td>
<td>1 drop = 7.19 mg/L Ca = 1°dH</td>
<td>1 drop = 7.19 mg/L Ca = 1°dH</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>1 - 12 mg/L</td>
<td>0.1 mL = 2 mg/L O²</td>
<td>0 - 10 mg/L</td>
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<tr>
<td>Sulfate</td>
<td>50 - 330 mg/L</td>
<td>40 - 200 mg/L</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfide</td>
<td>0.03 - 0.8 mg/L</td>
<td>0.03 - 0.8 mg/L</td>
<td></td>
<td></td>
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<tr>
<td>pH-value</td>
<td>4.5-10.0</td>
<td>5.0 – 9.0</td>
<td>5.0 – 9.0</td>
<td>4.5 - 10.0</td>
<td>6.8 - 8.2</td>
<td></td>
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<tr>
<td>No. of Parameters</td>
<td>17</td>
<td>5</td>
<td>6</td>
<td>6</td>
<td>9</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>Measurements by</td>
<td>Photometer &amp; Titrations</td>
<td>Color Chart &amp; Titrations</td>
<td>Color Chart &amp; Titrations</td>
<td>Color Chart &amp; Titrations</td>
<td>Photometer &amp; Titrations</td>
<td>Color Chart</td>
<td></td>
</tr>
</tbody>
</table>

* Additional Photometer needed - SPECTRO 2 or SPECTRO 3 - see page 22

www.sigma-aldrich.com/aquanal
The kits can be used for project work (as in training programs and schools) as well as for standard, routine measurements. They are supplied in sturdy cases that provide mobility and permit day-to-day routine and reliable handling. All kits come with a comprehensive manual explaining the function and practical handling of the tests. An important cost-savings attribute: individual test reagents can be refilled, rather than replacing the entire kit.

**AQUINAL® EduCase (Cat. No. 37518 or 37519*)**
The AQUINAL® EduCase was designed for teaching water titration as part of a classroom curriculum. The case contains reagents for titrimetric determination of five typical constituents in water that can be determined using four different types of titration: argentometric, complexometric, acidimetric and redox titration. Parameters determined are chloride, calcium and oxygen concentration, carbonate and total hardness.
* Refill pack

**AQUINAL®-Ökotest (Cat. No. 37557 or 37543*)**
The AQUINAL®-Ökotest Water Laboratory is especially suited to the individual user to test the quality of spring water, for example, or for use in schools as part of a water quality study project. The AQUINAL®-Ökotest Water Laboratory contains six tests on substances dissolved in water. The tests can be performed simply and rapidly with the help of the accompanying clear instructions. The individual reagents are environmentally safe, posing no threat to either the user or to environment.
* Kit with low level phosphate and nitrate test.

**AQUINAL®-plus Fishwater Lab (Cat. No. 37566)**
Nine important ingredients for a healthy aqueous living environment – ammonium, nitrate, nitrite, phosphate, oxygen, iron, carbonate hardness, pH and total hardness in water – can be determined directly in lakes, rivers, ponds and home aquariums using the AQUINAL®-plus Fishwater Lab. It contains six colourmetric and two titrimetric tests. The pH value is determined by pH paper.

**AQUINAL®-Case for Building Restoration (Cat. No. 37563)**
The analytical case for building restoration is designed for investigating the efflorescing of masonry, for aiding decontamination and renovation work and for analyzing water and efflorescence substances that may be harmful to buildings. The case contains tests for the determination of chloride, total hardness, magnesium, nitrate, sulfate and sulfide.

**AQUINAL®-plus Compact Lab (Cat. No. 37562)**
The AQUINAL®-plus Compact Lab is designed for the rapid analysis of 17 water parameters in the field where the samples are taken. The case contains all the reagents needed to carry out trace analysis for 16 contaminating substances as well as total hardness and pH. It also contains necessary equipment, including syringes, funnels, filters and collecting bottles. The AQUINAL®-plus Compact Lab is ideally suited to meet the requirements of fire brigades, police and environmental protection officers and local authorities. It is also suitable for use in schools.

**AQUINAL® Pooltester Chlorine/pH (Cat. No. 37546)**
The AQUINAL® Pooltester is a high-grade test kit with a wide measuring range for determination of both free chlorine and pH value. It is supplied in a practical, hinged box which can be conveniently hung near the pool. Results are read with a color comparator. The tests are easy to handle and can be performed by any user.

**AQUINAL® Vario Case (Cat. No. 37553)**
The flexible Vario Case allows users to assemble their own kits to measure any five parameters in the AQUINAL®-plus product range. The case consists of five test sets and, if chosen, a total hardness reagent and pH indicator sticks. The case itself, the total hardness reagent and the pH-indicator sticks are supplied free of charge.

The entire AQUINAL® water test line comprises nearly 40 test kits. For comprehensive information on all available AQUINAL® water tests, e.g. COD measurements and QUANTOFIX® test sticks, request our new AQUINAL® brochure or visit our Web site: www.sigma-aldrich.com/aquanal

If you have further questions, please contact your local Sigma-Aldrich technical service office, or send an email to aqualab@sidal.com.
A sophisticated solution for water analysis:

AQUANAL®-SPECTRO 3 Photometer

Operating in both UV and infrared spectral ranges, AQUANAL®-SPECTRO 3 Photometer has many features that make it flexible, accurate, reliable and easy to operate.

**Flexibility**
- For both AQUANAL®-plus and AQUANAL®- professional reagents
- Operates in both UV and infrared spectral ranges
- Built-in user prompts in six languages
- Wide spectral range: 380 / 430 / 470 / 500 / 520 / 560 / 610 / 700 / 810 nm
- Wide absorbance range: -0.500 to 3.500 Abs
- Test result displayed in mg/L or in extinction mode
- Software operates with Windows 98 and higher versions

**Accuracy & Reliability**
- Electro-optical accuracy: ±1.5 %
- Combined LED and fiber-optic technology
- GLP compliant (results given with time / date / place)
- Comprehensive recognition of measurement faults
- Data memory for 1000 results, with data protection

To get you up and running quickly, the SPECTRO 3 is supplied with
- Software (operates with Windows 98 and higher versions)
- External power pack
- Four rechargeable batteries (1.5 V)
- Infrared interface
- Funnel
- Six 16 mm ID tubes
- Four 20 mL sample tubes
- USB to IrDA adapter
- Carrying case
- Instruction manual

www.sigma-aldrich.com/aquanal
New Product Corner ....... Allergenic dispersion dye standards

By Ingrid Hayenga, Senior Scientist R&D Applications, Fluka ... ihayenga@europe.sial.com

Dispersion dyes are used for dying synthetic fibers. Approximately twenty different dyes used in textiles are known to cause an allergenic effect on skin, originally called "nylon allergy," although the contact dermatitis was caused by dyes and not by nylon. It is estimated that 4-5% of the population can be contact sensitized from textiles. The general threshold value is < 5 mg/L. From this group of dispersion dyes, 9 dyes are prohibited in the European Union (EU). For reliable identification and quantification of dispersion dyes, which is typically carried out by LC-MS, it is necessary to have pure, well characterized reference standards. Sigma-Aldrich offers you the first bundle of five dispersion dye standards with high purity (≥ 96%) for this application.

<table>
<thead>
<tr>
<th>Cat. No.</th>
<th>Brand</th>
<th>Description</th>
<th>Package Size</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>11344</td>
<td>Fluka</td>
<td>Disperse Yellow 3</td>
<td>25 mg</td>
<td>prohibited in the EU</td>
</tr>
<tr>
<td>38464</td>
<td>Fluka</td>
<td>Disperse Yellow 9</td>
<td>25 mg</td>
<td></td>
</tr>
<tr>
<td>29173</td>
<td>Fluka</td>
<td>Disperse Orange 1</td>
<td>25 mg</td>
<td></td>
</tr>
<tr>
<td>42994</td>
<td>Fluka</td>
<td>Disperse Orange 11</td>
<td>25 mg</td>
<td></td>
</tr>
<tr>
<td>11074</td>
<td>Fluka</td>
<td>Disperse Red 1</td>
<td>25 mg</td>
<td>prohibited in the EU</td>
</tr>
</tbody>
</table>

Vial Silanization Service ....... Maintain sample integrity, reduce adsorption and save time

By Vicki Yearick, Environmental Market Segment Manager ... vyearick@sial.com

Samples containing pesticides, amines, drugs and other reactive compounds should be stored in silanized glass vials to preserve sample integrity. Untreated glass surfaces have high concentrations of silanol groups, which can serve as catalytic centers for decomposition of unstable compounds and create hydrogen bonds with polar compounds, resulting in adsorption. Quantitative analyses of active compounds stored in untreated vials can become problematic. Pre-treating the glass vials before use will prevent these problems.

Problems with do-it-yourself silanization

There are a variety of silanization products available in the marketplace for pre-treating glass. All are hazardous and require care during handling and for disposal. Identifying a silanization procedure that will adequately treat a vial can be time consuming. Treating a large quantity of vials at one time may require dedicated lab space, the use of large volumes of solvent and unexpected equipment purchases. All of these factors can significantly increase your laboratory's operating costs.

Our silanization service saves time and resources

Sigma-Aldrich's commercial vial silanization service will save you time, lab space and money. Our two-step silanization process uses organosilanes and gives a more homogenous, inert and hydrophobic glass surface. Residual, unreacted silanol groups are shielded, preventing contact with the chemicals stored in the vial.

Solvent-free and environmentally-friendly

Our silanization process uses no solvents and employs an elaborate trapping system that prevents the release of toxic silanization agent vapors. It is also highly automated, thereby reducing costs.

Silanization service for nearly all types of vials

We have experience silanizing vials ranging from 2 mL to 40 mL, and maintain a stock of popular 2 mL and 4 mL silanized vials. If your application requires a different vial, you may choose from the large assortment of Supelco brand vials, or send us your own vials for treatment. To obtain a quote or learn more about our silanization process, please contact our Technical Service department at techservice@sial.com.
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