

Analytix

Advances in Analytical Chemistry

Issue 3 • 2006

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Determination of Organic Acids

Standards

- Organic Acid Standards
- Phenolic Standards
- Acetamide Herbicide Standards

Sensorics

- Optical Sensors for Alcohols and Amines

Titration

- Water Determination in Biodiesel
- New HYDRANAL® Manual

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Innovation We provide practical innovative solutions for our customers



Picture Michael Jeitziner,
Market Segment Manager,
Analytical Reagents

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



Picture

We provide innovative solutions to scientists

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Determination of organic acids in wine and fruit juices with ion exclusion chromatography Fluka brand standard solutions ensure reliable quantification

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

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 1 Organic acid standard solutions, HPLC columns and SPE tubes

Cat. No.	Brand	Description	Remarks	Package Size
13669	Fluka	Acetate Ion Chromatography Standard Solution	1.000 g/L in H ₂ O	100 mL
38730	Fluka	Citrate Ion Chromatography Standard Solution	1.000 g/L in H ₂ O	100 mL
49897	Fluka	Formate Ion Chromatography Standard Solution	1.000 g/L in H ₂ O	100 mL
49323	Fluka	Malonate Ion Chromatography Standard Solution	1.000 g/L in H ₂ O	100 mL
04621	Fluka	Oxalate Ion Chromatography Standard Solution	1.000 g/L in H ₂ O	100 mL
79409	Fluka	Phosphate Ion Chromatography Standard Solution	1.000 g/L in H ₂ O; traceable to BAM	100 mL
04924	Fluka	Phthalate Ion Chromatography Standard Solution	1.000 g/L in H ₂ O	100 mL
02717	Fluka	Propionate Ion Chromatography Standard Solution	1.000 g/L in H ₂ O	100 mL
50824	Fluka	Tartrate Ion Chromatography Standard Solution	1.000 g/L in H ₂ O	100 mL
57089	Supelco	Supelclean™ LC-4 SPE Tube	Wide pore, bed wt. 500 mg, volume 3 mL	54 tubes per package
59320-U	Supelco	SUPELCOGEL™ C-610H	30 cm x 7.8 mm ID, particle size 9 µm	Each
59319	Supelco	SUPELCOGEL™ H Guard Column	5 cm x 4.6 mm ID	Each

Figure 1 Organic acid standards (after SPE)

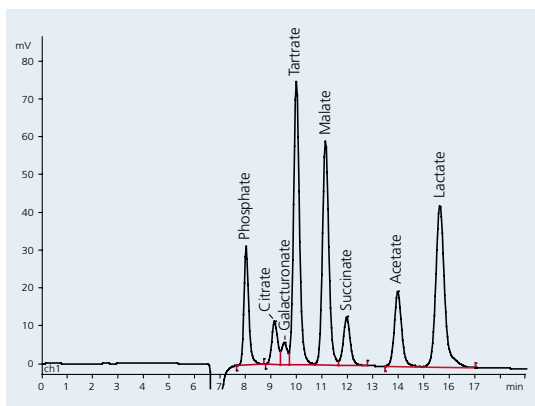
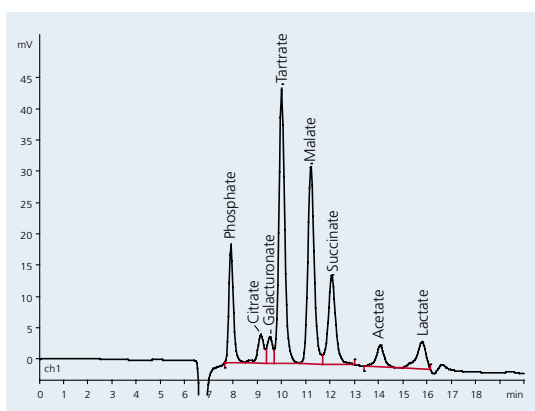


Figure 2 Organic acids in white wine 1, Müller-Thurgau (after SPE)



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

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.

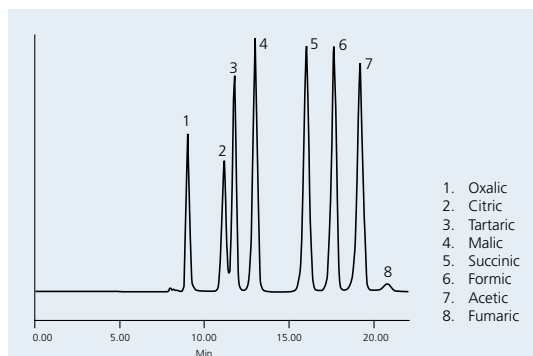


Figure 3 Organic Acid Standards Mix (10 µL injected)

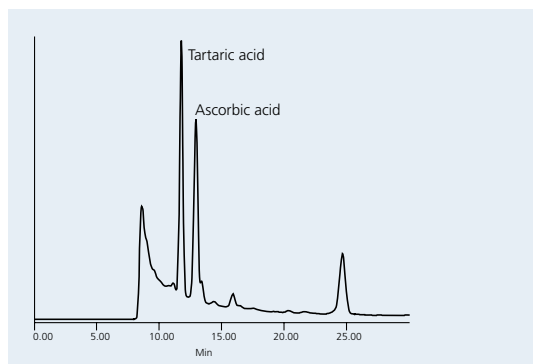


Figure 4 Grape Juice Cocktail (10 µL injected)

Conditions (Figures 3 and 4):

Column: SUPELCOGEL C-610H, 30 cm x 7.8 mm ID (Cat. No. 59320-U)
Mobile Phase: 0.1% H₃PO₄
Col. Temp.: 30°C; **Flow Rate:** 0.5 mL/min; **Det.:** UV 210 nm

Optical Sensors for Alcohols and Amines Sigma-Aldrich offers a complete line of Fluka-brand Selectophore® compounds for quantification of alcohols and amines in aqueous solution

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^T 4001 whose applicability for alcohol monitoring has already been evaluated in detail by the Centre for Chemical Sensors in Technopark Zurich.

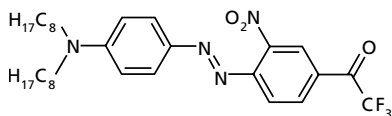


Figure 1 Chromoreactant CR-546 (*N,N*-dioctylamino-4'-trifluoroacetyl-2'-nitroazobenzene) Fluka Cat. No 08709, Selectophore®

Apparatus

The detection apparatus (see **Figure 2**) comprises the sensor layers, prepared as described below, fixed in a flow-through cell that permits detection of color changes through an optical window in the center of the cell using a conventional spectrophotometer or a fiber optic spectrophotometer. Simultaneously, using a peristaltic pump, the analyte solution is pumped through the cell via the tubing attached below and above the cell. The sample stream is in continuous contact with the sensor layer and any color changes due to changing analyte concentrations can be monitored. The correlation between changes in absorbance and analyte concentration allows quantification of the analyte in the sample solution.

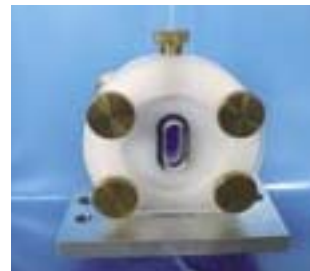


Figure 2
Flow-through chemical-sensing optical detector for analyte streams



Figure 3
Differential color change on an optical sensor disk upon deposition of analyte solution

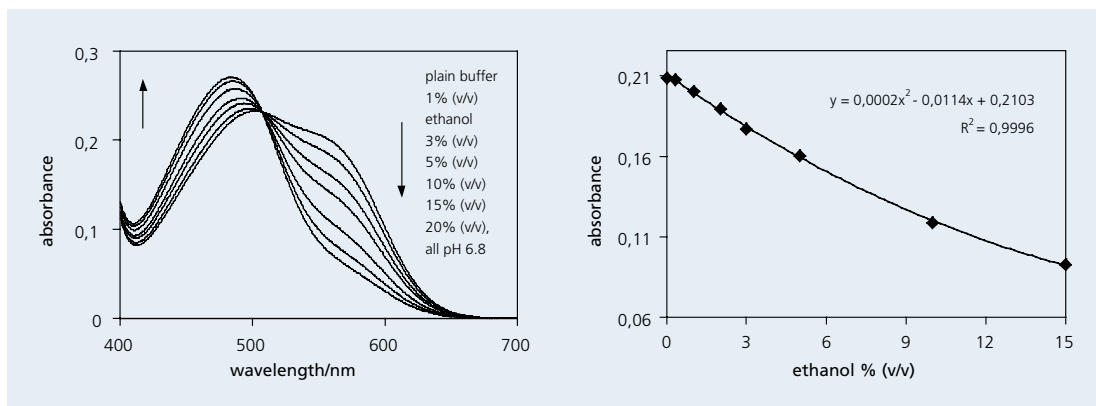
Preparation of an absorbance-based sensor layer for alcohols

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 chromoreactant *N,N*-dioctylamino-4'-trifluoroacetyl-2'-nitroazobenzene (Chromoionophore XVI), which undergoes a reversible chemical reaction with alcohols giving a simultaneous color change. The chromoreactant 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.

Figure 4 Change in absorption of optical sensing layer as a function of wavelength (left panel) or ethanol concentration (right panel)

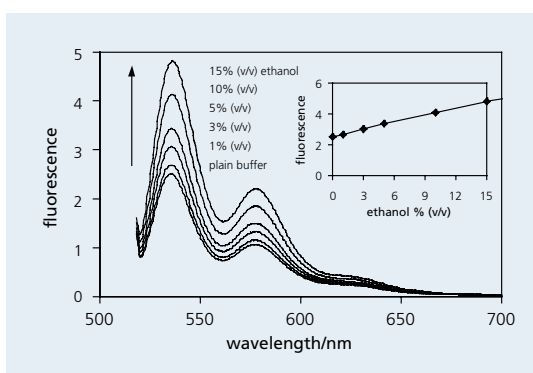


The sensor layers are compatible with the green LED as a light source which allows the development of miniaturized devices based on CMOS (complementary metal oxide semiconductor) technology. The layers have better operational life and shelf-life than enzyme based sensors for alcohols, with lifetimes 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 trifluoroacetyl form of CR-546, with its maximum at around 560 nm, overlaps the emission of the fluorophore. Increasing ethanol concentrations causes decreasing 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.

Figure 5 Change in fluorescence spectra as a function of wavelength and ethanol concentration (inset).



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 Ethanol-containing samples evaluated with the fluorescence-based sensor layer

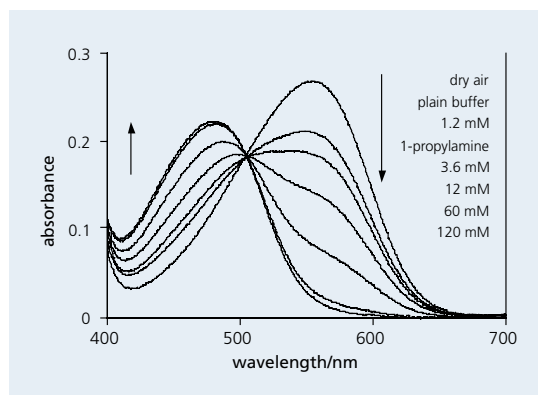
Sample	Reported [% (v/v)]	Found [% (v/v)]
Leikheim Premium beer	4.9	5.0 +/- 0.4
Torgauer Landbier	5.5	5.6 +/- 0.2
Blanchet white wine	11.0	11.1 +/- 0.2
Amsfelder Lieblich red wine	11.0	11.3 +/- 0.3
Blanchet Syrah red wine	12.5	11.8 +/- 0.4

Absorbance-based optical amine sensor

The chromoreactant *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.

Figure 6 Change in absorbance of the optical sensor as a function of wavelength and 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 (tridodecylmethylammonium 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

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- [3] Mohr, G. J.; Zhylyak, G.; Nezel, T.; Spichiger, U. E.; Kerness, N.; Brand, O.; Baltes, H.; Grummt, U.-W.; Using reactands in CMOS-based calorimetric sensors: New functional materials for electronic noses. *Analytical Sciences*, **2002**, *18*, 109-112.

Product Listing Selectophore® optical sensor compounds from Sigma-Aldrich

Cat. No.	Brand	Description	Package Size
08709	Fluka	<i>N,N</i> -diethylamino-4'-trifluoroacetyl-2'-nitroazobenzene (Chromoreactand CR-546) Selectophore®	10 mg, 50 mg
91661	Fluka	Tridodecylmethylammonium chloride Selectophore®	100 mg, 1 g
16459	Fluka	<i>N,N'</i> -bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (S-13)	1 mg, 10 mg
73732	Fluka	2-Nitrophenyl octyl ether (NPOE) Selectophore®, $\geq 99.0\%$ (GC)	5 mL, 25 mL, 100 mL
81392	Fluka	Poly(vinyl chloride) (PVC) Selectophore®, high molecular weight	1 g, 10 g, 50 g
87369	Fluka	Tetrahydrofuran (THF) Selectophore®, $\geq 99.5\%$ (GC)	10 mL, 100 mL, 500 mL

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.

Table 1 Phenolic compound standards from Sigma-Aldrich

Cat. No.	Brand	Description	Pack Size
48859	Supelco	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)	1 mL
		2,4-Dichlorophenol (500 µg/mL) Phenol (500 µg/mL) 2,4-Dimethylphenol (500 µg/mL) 2,4,6-Trichlorophenol (1500 µg/mL)	
		2,4-Dinitrophenol (1500 µg/mL) 4-Nitrophenol (2500 µg/mL) 2-Methyl-4,6-dinitrophenol (2500 µg/mL)	
47899	Supelco	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	1 mL
		2,3,5-Trichlorophenol 2,6-Dichlorophenol 4-Nitrophenol 2,3,6-Trichlorophenol 2,4-Dimethylphenol Pentachlorophenol 2,4,5-Trichlorophenol 2,4-Dinitrophenol	
		Phenol 2,4,6-Trichlorophenol 2-Methyl-4,6-dinitrophenol 2,3,4,5-Tetrachlorophenol 3,4,5-Trichlorophenol 2-Methylphenol 2,3,4,6-Tetrachlorophenol	
48130-U	Supelco	MISA Group 20 Phenols Mix A, 2000 µg/mL each in methanol: o-Cresol 2,3,4,6-Tetrachlorophenol p-Cresol 2,3,5,6-Tetrachlorophenol	1 mL
		2,6-Dichlorophenol 2,3,4-Trichlorophenol 2,4-Dimethylphenol	
		2,3,5-Trichlorophenol 4,6-Dinitro-o-cresol 2,4,5-Trichlorophenol	
48131	Supelco	MISA Group 20 Phenols Mix B, 2000 µg/mL each in methanol: p-Chloro-m-cresol 4-Nitrophenol m-Cresol Pentachlorophenol	1 mL
		2-Chlorophenol Phenol 2,4-Dichlorophenol	
		2,3,4,5-Tetrachlorophenol 2,4-Dinitrophenol 2,4,6-Trichlorophenol	
861253	Supelco	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	1 mL
		2,6-Dichlorophenol Pentachlorophenol 2,4-Dimethylphenol Phenol 2,4-Dinitrophenol 2,3,4,6-Tetrachlorophenol	
		2-Methyl-4,6-dimethylphenol 2,4,5-Trichlorophenol 2-Methylphenol 2,4,6-Trichlorophenol 3-Methylphenol (1000 µg/mL)	

Please visit our web site: 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

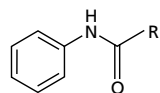


Figure 1
The Acetanilide Moiety

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, acetochlor, metolachlor, propachlor, dimethenamid and flufenacet. These compounds undergo environmental degradation to more polar, and more water soluble, ethanesulfonic acid (ESA), oxanilic acid (OA) and sulfinylacetic 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 matrixes. 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)

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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.

Product Listing EPA Method 535 Pesticide Analyte Standards

Cat. No.	Brand	Description
34145	Pestanal (Riedel-de Haën)	Acetochlor-ESA
34144	Pestanal (Riedel-de Haën)	Acetochlor-OA
34147	Pestanal (Riedel-de Haën)	Alachlor-ESA
34146	Pestanal (Riedel-de Haën)	Alachlor-OA
34153	Pestanal (Riedel-de Haën)	Flufenacet-ESA
34154	Pestanal (Riedel-de Haën)	Flufenacet-OA
34149	Pestanal (Riedel-de Haën)	Metolachlor-ESA
34148	Pestanal (Riedel-de Haën)	Metolachlor-OA
34152	Pestanal (Riedel-de Haën)	Propachlor-ESA
34151	Pestanal (Riedel-de Haën)	Propachlor-OA

Package Size each 10 mg

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. 581303-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.

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



Introduction

Escalating oil prices, concerns over its reliable supply and the persistent environmental problems associated with the extraction, production, transport, refinement and combustion of oil and its byproducts have driven research into alternate fuel sources. In the last decade, there has been increased interest in biodiesel, which is derived from renewable sources, such as vegetable oils and animal fats, and conforms to ASTM D6751 and EN-14214 specifications for use in diesel engines. Sigma-Aldrich has recently introduced a number of biodiesel standards for EN 14105 and ASTM D6584 (1).

One practical problem with biodiesel is its hydrophilicity. Some of the water is derived from processing, while some comes from condensation within the storage tank. The presence of water in biodiesel poses a problem for a number of reasons:

- Water reduces the heat of combustion. This means more smoke, harder starting and less power.
- Water will corrode vital fuel system components, like fuel pumps, injector pumps, fuel lines, etc.
- As water approaches 0 °C (32 °F), it begins to form ice crystals. These crystals provide sites of nucleation and accelerate the gelling of the residual fuel.
- Water is required for the growth of most microbes. Biodiesel is an ideal nutrient base for microbes and the presence of water accelerates the growth of microbe colonies, which can clog fuel systems. Biodiesel users who have heated fuel tanks face a year-round microbial growth problem.

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.

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

- [1] Analytix Issue 4-2005; www.sigma-aldrich.com/analytix
[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 Selected **HYDRANAL®** Products (see www.sigma-aldrich.com/hydranal for the complete list)

Cat. No.	Brand	Product	Used as...
34806	Riedel-de Haën	HYDRANAL® Composite 2	One component reagent, titre: 1 mL ~ 2 mg water
37855	Riedel-de Haën	HYDRANAL® LipoSolver CM	To use with HYDRANAL® Composite for titration of non-polar substances, fats and oils
37856	Riedel-de Haën	HYDRANAL® LipoSolver MH	To use with HYDRANAL® Composite for titration of non-polar substances, fats and oils
34734	Riedel-de Haën	HYDRANAL® CompoSolver E	Methanol-free working medium
37817	Riedel-de Haën	HYDRANAL® Methanol Rapid	Solvent for a fast Karl-Fischer titration, max. 0.02% water
34807	Riedel-de Haën	HYDRANAL® Coulomat A	Anolyte for cells with diaphragm, reagent contains chloroform
34868	Riedel-de Haën	HYDRANAL® Coulomat Oil	Anolyte for titration of oils
34843	Riedel-de Haën	HYDRANAL® Coulomat AG-H	Anolyte for titration of long-chained hydrocarbons free of halogenated hydrocarbons
34739	Riedel-de Haën	HYDRANAL® Coulomat AG Oven	Anolyte for determination with KF-oven
34840	Riedel-de Haën	HYDRANAL® Coulomat CG	Catholyte, free of halogenated hydrocarbons, 25 mL bottle resp. 10 x 5 mL ampoules
34847	Riedel-de Haën	HYDRANAL® Water Standard 0.10	1 g contains 0.10 mg = 0.01 % water, contains 10 glass ampoules of 4 mL, traceable to NIST SRM 2890
34241	Riedel-de Haën	HYDRANAL® Molecular sieve 0.3 nm	Drying agent for Karl Fischer applications

**Technical Support**

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

Europe and Rest of the World

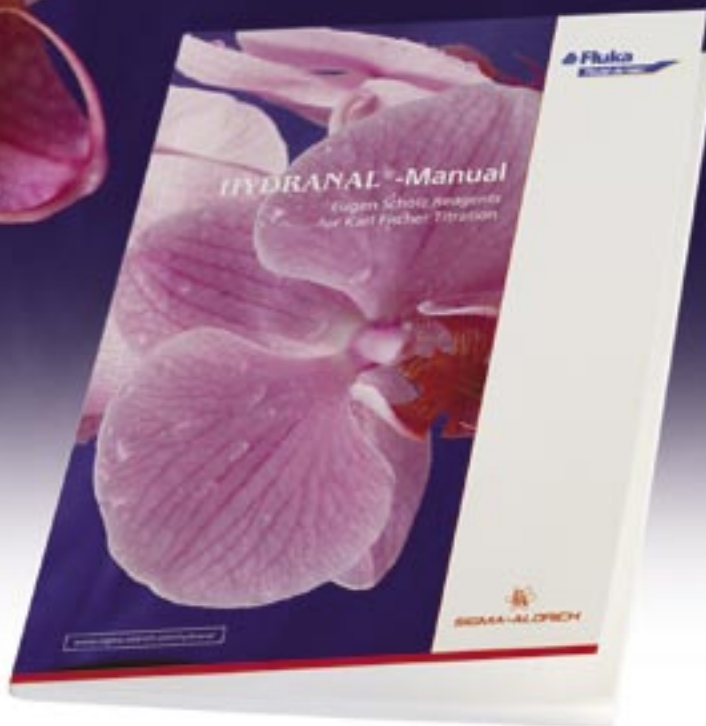
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- Sample handling techniques
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Lewatit® Ion Exchange Resins – All-around Solutions for Chemical Processes

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

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

Figure 1

Thorough quality check of Lewatit® ion exchangers in a modern production site in Bitterfeld, Germany



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.

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



Figure 2
Monodispersed beads:
Each one equipped
with equal size,
pore structure and
functionalization

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 NH_3 , while alkali ion exchange resins adsorb acidic gases, such as HCl and SO_2 . 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 Lewatit® ion exchange resins properties and applications

Cat. No.	Description	Remarks	Application
62103	Lewatit® MonoPlus TP-207	Weakly acidic, macroporous cation exchange resin with chelating imino-diacetate groups	Selective binding of heavy metal ions from weakly acidic to weakly basic solutions
62108	Lewatit® MonoPlus TP-260	Weakly acidic, macroporous cation exchange resin with chelating aminomethyl phosphonic acid groups	(1) Refined purification of alkali chloride brines; (2) extraction/recycling of heavy metal ions
62105	Lewatit® MonoPlus TP-208	Weakly acidic, macroporous cation exchange resin with chelating imino-diacetate groups	Selective binding of alkaline earth ions and heavy metal ions
62107	Lewatit® MonoPlus TP-214	Monospherical, macroporous chelating resin with thiourea groups	Removal of Hg/Ag/Au/Pt from aqueous solutions
62084	Lewatit® MonoPlus K-2629	Strongly acidic macroporous polymer-based resin in spherical bead-form with sulfonic acid groups	(1) heterogenous catalyst for organic reactions (e.g. esterification, etherification) (2) processing of aqueous and organic liquids
17293	Lewatit® VP OC-1131	Cation exchange resin crosslinked polystyrene matrix with adsorbed di-2-ethylhexylphosphate	Removal of heavy metal ions from acidic and neutral solutions

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.

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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).

Table 1 LC-MS additives

Cat. No.	Brand	Description*	Package Size	Packaging
40967	Fluka	Trifluoroacetic acid, puriss p.a., eluent additive for LC-MS	50 mL	HDPE bottle
40967	Fluka	Trifluoroacetic acid, puriss p.a., eluent additive for LC-MS	10 x 1 mL	Glass Ampoules
56302	Fluka	Formic acid, puriss p.a., eluent additive for LC-MS	50 mL	HDPE bottle
49199	Fluka	Acetic acid, puriss p.a., eluent additive for LC-MS	50 mL	HDPE bottle
49916	Fluka	Propionic acid, puriss p.a., eluent additive for LC-MS	50 mL	HDPE bottle
55674	Fluka	Ammonium formate, puriss p.a., eluent additive for LC-MS	50 g	HDPE bottle
49638	Fluka	Ammonium acetate, puriss p.a., eluent additive for LC-MS	50 g	HDPE bottle
61333	Fluka	Sodium citrate tribasic dihydrate, puriss p.a., eluent additive for LC-MS	50 g	HDPE bottle
40867	Fluka	Ammonium bicarbonate, puriss p.a., eluent additive for LC-MS	50 g	HDPE bottle
44273	Fluka	Ammonium hydroxide solution 25%, puriss p.a., eluent additive for LC-MS	100 mL	HDPE bottle
65897	Fluka	Triethylamine, puriss p.a., eluent additive for LC-MS	50 mL	HDPE bottle

*"puriss" quality grade is defined as >98.5% assay, <0.1% ash, and specification n + 0.001, d + 0.001 with no extraneous color and a homogeneous appearance. "p.a." or *pro analysi* denotes a product with guaranteed trace impurity levels and/or suitability for the indicated analytical application.

Table 2 Selection of LC-MS solvents and blends

Cat. No.	Brand	Solvent or Blend Description	Package Size	Packaging
34965	Riedel-de Haën	2-Propanol Chromasolv LC-MS	1 L, 2.5 L	Amber glass bottle
34677	Riedel-de Haën	Water with 0.1% formic acid and 0.01% TFA	2.5 L	Amber glass bottle
34676	Riedel-de Haën	Acetonitrile with 0.1% formic acid and 0.01% TFA	2.5 L	Amber glass bottle

Table 3 Components of the peptide mixture

Cat. No.	Brand	Component	Molecular Mass	Mol. ion / Charge
B4181	Sigma	Bradykinin fragm. 1-7	756.4	[M+H] ⁺ / 1
A8846	Sigma	Angiotensin II	1045.5	[M+2H] ²⁺ / 2
P2613	Sigma	P ₁₄ R	1532.9	[M+2H] ²⁺ / 2
A8346	Sigma	ACTH fragm. 18-39	2464.2	[M+3H] ³⁺ / 3
I 6154	Sigma	Insulin oxid. B chain	3493.7	[M+3H] ³⁺ / 3

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=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⁺ adducts (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 Apffel 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;

Figure 1

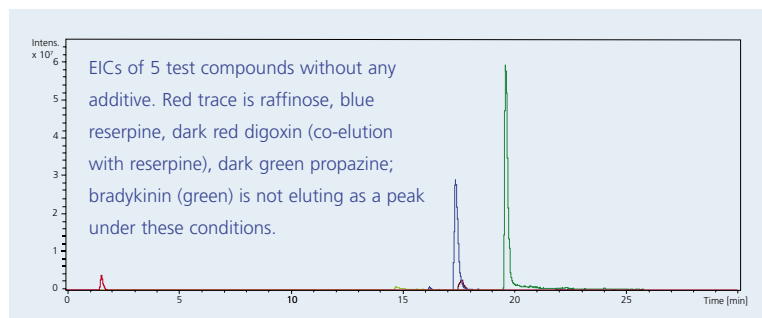


Figure 2

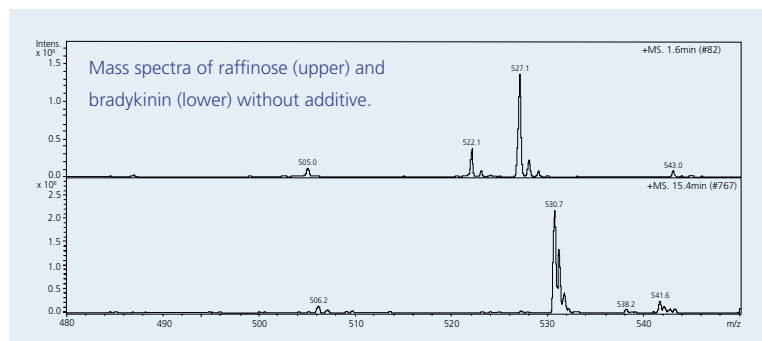
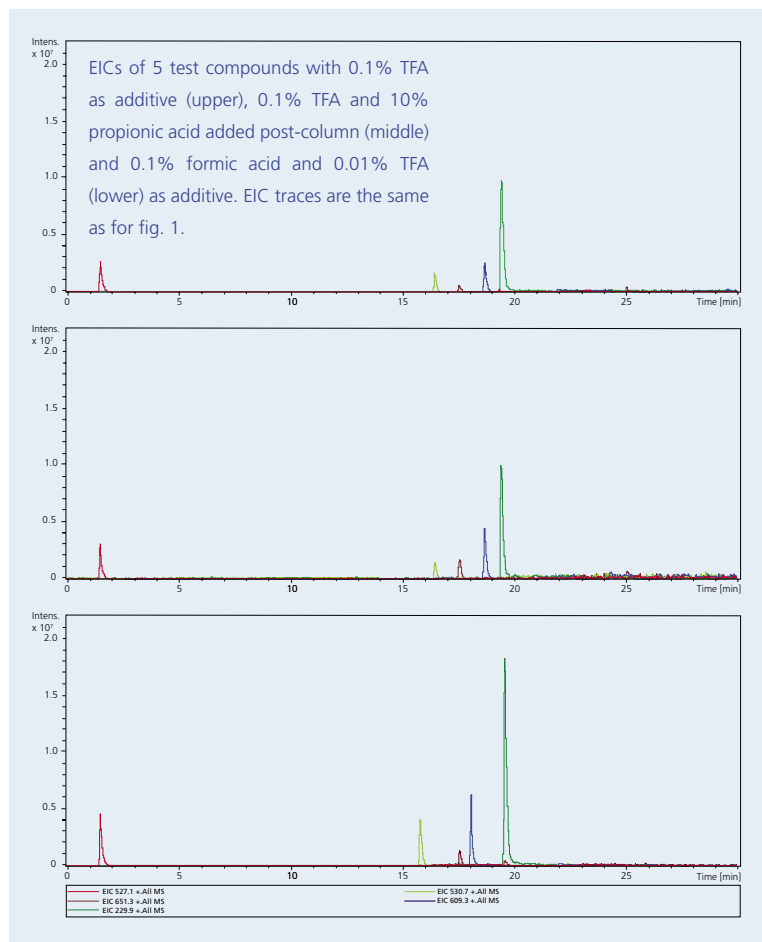


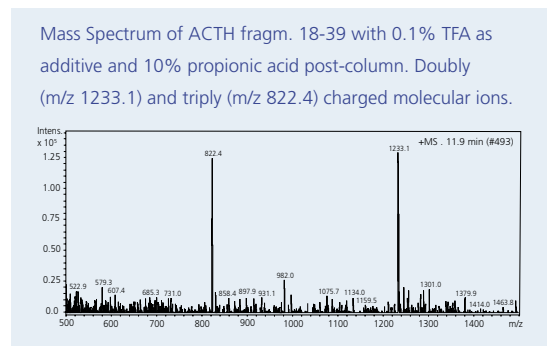
Figure 3



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.

Figure 4



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www.sigma-aldrich.com/analytix

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

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and Alex Rueck, Scientist R&D Fluka / Riedel-de-Haën

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

High Purity MALDI Matrices

Cat. No.	Brand	Product	Package Size
39468	Fluka	α -Cyano-4-hydroxycinnamic acid (HCCA) puriss. p.a., $\geq 99.5\%$ (HPLC)	10 x 10 mg
39319	Fluka	2,5-Dihydroxybenzoic acid (Gentisic acid) puriss. p.a., $\geq 99.5\%$ (HPLC)	10 x 10 mg
49508	Fluka	Sinapic acid puriss. p.a.	10 x 10 mg

ProteoMass™ MALDI-MS Peptide Standards

Cat. No.	Brand	Product	Package Size
P2613	Sigma	ProteoMass™ P14R MALDI-MS Standard	5 x 10 nmol
B4181	Sigma	ProteoMass™ Bradykinin Fragment 1-7	5 x 10 nmol
A8846	Sigma	ProteoMass™ Angiotensin II	5 x 10 nmol
A8346	Sigma	ProteoMass™ ACTH Fragment 18-39	5 x 10 nmol
I6154	Sigma	ProteoMass™ Insulin chain B oxidized	5 x 10 nmol

LUCY™ Fluorescent Dyes (5 mg/mL in DMSO, 5000 X Stock solution)

Cat. No.	Brand	Product	Package Size
14149	Fluka	LUCY- 506	500 μ L
43772	Fluka	LUCY- 565	500 μ L
41629	Fluka	LUCY- 569	500 μ L

Figure 1
Comparison of
MALDI-MS spectra
provided by ultra-pure
and regular grade
HCCA

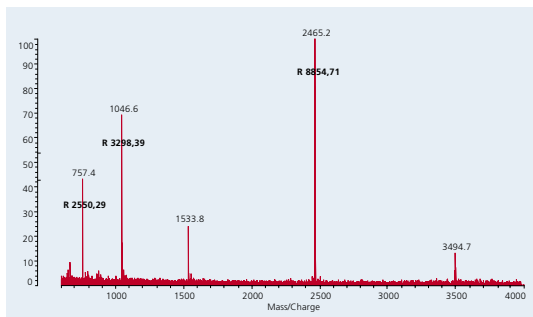


Figure 1a HCCA Ultra-pure grade (Cat. No. 39468)

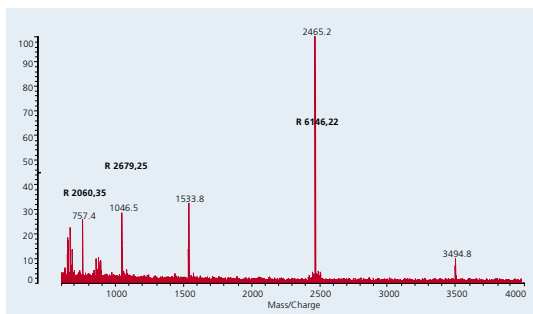


Figure 1b HCCA regular grade

Sample: 0.7 μ L ProteoMass™ peptide mix (bradykinin (1.5 μ M), angiotensin II (1.0 μ M), P14R (0.5 μ M), ACTH (1.0 μ M), insulin B-chain (2.0 μ M), mixed with 0.7 μ L 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

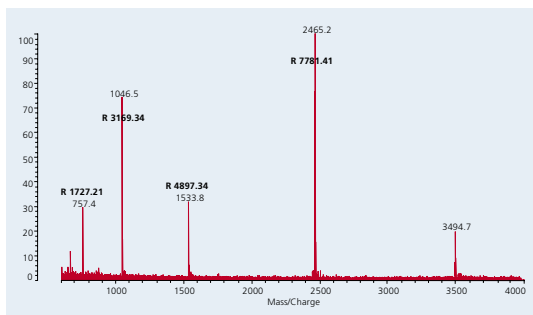


Figure 2a HCCA Ultra-pure grade (Cat. No. 39468)

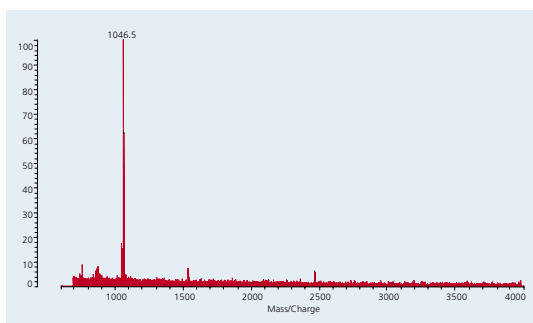


Figure 2b HCCA regular grade

Sample: 0.7 μ L 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 μ L HCCA matrix in AcN/0.1%TFA
MALDI-MS: Kratos PC Axima, reflectron mode, laser power 85%.

Figure 1. Note that the use of the ultra-pure HCCA matrix resulted in significantly higher peak resolution. Even when the peptide standard sample was diluted 10-fold (**Figure 2**), the use of ultra-pure HCCA provides a clear spectrum with resolution comparable to the more concentrated sample. In contrast, the standard quality HCCA did not yield a suitable spectrum.

Perfect MALDI companion: High sensitivity LUCY™ fluorescent dyes

For analyzing peptides from enzymatic digest, separated by 1D or 2D-gels, as in proteomics experiments, not only must the MALDI matrix be of high purity, but the dyes used to stain the gels prior to excising the spots must allow visualization of low abundant proteins. The Fluka-brand LUCY™ fluorescent dyes from Sigma-Aldrich meet this requirement. Figure 3 shows a typical example. A 100 ng band of β -galactosidase was excised from a 1D-gel which was stained with Lucy 506. After trypsin digest and peptide extraction, using the Trypsin Profile IGD kit (no. PPO100), MALDI-MS was performed by mixing peptides with ultra pure HCCA matrix. The protein could be identified by database analysis and peptide mass finger print. The resulting MALDI mass spectrum is shown in **Figure 3**.

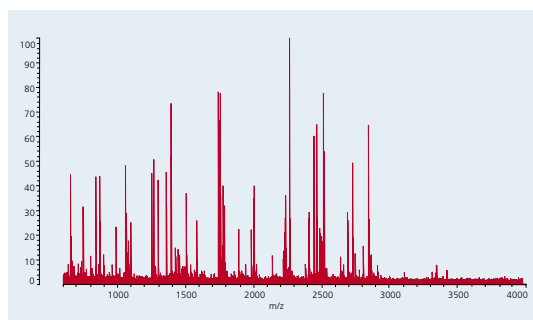


Figure 3 Ultra-pure HCCA MALDI-MS spectrum of β -Galactosidase digest, excised 1D-gel band following LUCY-506 staining

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

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

Lab Type	Compact Lab*	EduCase	Ökotest Water Lab	Ökotest Water Lab Low Phosphate	Fishwater Lab	Analytical Case for Building Restoration*	Pool tester
Cat.No.	37562	37518	37557	37543	37566	37563	37546
Ammonium	0.2 - 8.0 mg/L		≤ 0.05 - 10 mg/L	≤ 0.05 - 10 mg/L	≤ 0.05 - 10.0 mg/L		
Calcium		0.1 mL = 14.2 mg/L Ca					
Carbonate Hardness		0.1 mL = 2°CH			1 drop = 1°CH		
Chloride	5 - 300 mg/L	0.1 mL = 20 mg/L Cl				2 - 100 mg/L	
Chlorine	0.01 - 0.3 mg/L						0.1 - 6.0 mg/L
Chromium	0.005 - 0.1 mg/L						
Copper	0.05 - 4.5 mg/L						
Cyanide (total)	0.03 - 0.7 mg/L						
Iron	0.2 - 15 mg/L				< 0.05 - 1.0 mg/L		
Magnesium						100 - 1,500 mg/L	
Nickel	0.02 - 0.5 mg/L						
Nitrate	1 - 50 mg/L		10 - 80 mg/L	0.5 - 50 mg/L	10 - 80 mg/L	0.5 - 50 mg/L	
Nitrite	0.005 - 0.1 mg/L		0.02 - 1.0 mg/L	0.02 - 1.0 mg/L	≤ 0.02 - 1.0 mg/L		
Phenol	0.1 - 3.0 mg/L						
Phosphate	0.02 - 0.4 mg/L		0.5 ≥ 6.0 mg/L	0.02 - 0,4 mg/L	0.5 ≥ 6.0 mg/L		
Total hardness	1 drop = 1°dH	0.1 mL = 20 mg/L CaO = 2° dH	1 drop = 7.19 mg/L Ca = 1°dH	1 drop = 7.19 mg/L Ca = 1°dH	1 drop = 7.19 mg/L Ca = 1°dH	1 drop = 7.19 mg/L Ca = 1°dH	
Oxygen	1 - 12 mg/L	0.1 mL = 2 mg/L O ²			0 - 10 mg/L		
Sulfate	50 - 330 mg/L					40 - 200 mg/L	
Sulfide	0.03 - 0.8 mg/L					0.03 - 0.8 mg/L	
pH-value	4.5-10.0		5.0 - 9.0	5.0 - 9.0	4.5 - 10.0		6.8 - 8.2
No. of Parameters	17	5	6	6	9	6	2
Measurements by	Photometer & Titration	Titration	Color Chart & Titration	Color Chart & Titration	Color Chart & Titration	Photometer & Titration	Color Chart

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



AQUANAL® EduCase



AQUANAL®-Ökotest



AQUANAL®-plus Fishwater Lab



AQUANAL®-Case for Building Restoration



AQUANAL®-plus Compact Lab



AQUANAL® Pooltester



AQUANAL® Vario Case

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.

AQUANAL® EduCase (Cat. No. 37518 or 37519*)

The AQUANAL® 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

AQUANAL®-Ökotest (Cat. No. 37557 or 37543*)

The AQUANAL®-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 AQUANAL®-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.

AQUANAL®-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 AQUANAL®-plus Fishwater Lab. It contains six coulometric and two titrimetric tests. The pH value is determined by pH paper.

AQUANAL®-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.

AQUANAL®-plus Compact Lab (Cat. No. 37562)

The AQUANAL®-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 AQUANAL®-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.

AQUANAL® Pooltester Chlorine/pH (Cat. No. 37546)

The AQUANAL® 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.

AQUANAL® Vario Case (Cat. No. 37553)

The flexible Vario Case allows users to assemble their own kits to measure any five parameters in the AQUANAL®-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 AQUANAL® water test line comprises nearly 40 test kits. For comprehensive information on all available AQUANAL® water tests, e.g. COD measurements and QUANTOFIX® test sticks, request our new AQUANAL® 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 aquanal@sial.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: $\pm 1.5\%$
- 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

Convenience

- Selection of the most frequently used curves
- Built-in calibration curves for 100 determinations
- Automatic blank setting
- History view lists the latest 50 results
- Power-saving function, automatic power off
- Automatic wavelength selection

AQUANAL[®]-SPECTRO 3 Photometer comes with all you need to get started



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

New Product Corner Allergenic dispersion dye standards

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



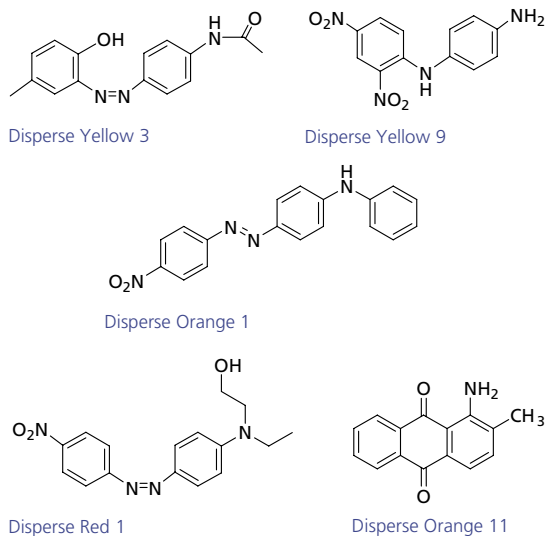
Dispersion dyes are used for dyeing synthetic fibers. Approximately twenty different dyes used in textiles are known to cause an allergenic effect on skin, originally called "nylon allergy," although the contact dermatitis was caused by dyes and not by nylon.

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 ($\geq 96\%$) for this application.

Figure 1 Dispersion dye structures



Cat. No.	Brand	Description	Package Size	Remark
11344	Fluka	Disperse Yellow 3	25 mg	prohibited in the EU
38464	Fluka	Disperse Yellow 9	25 mg	
29173	Fluka	Disperse Orange 1	25 mg	
42994	Fluka	Disperse Orange 11	25 mg	
11074	Fluka	Disperse Red 1	25 mg	prohibited in the EU

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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