

Speciation ICP-MS

Altus LC, Clarus GC, NexION, Empower

Simone Korstian

Analytica 2016



HUMAN HEALTH • ENVIRONMENTAL HEALTH



AAS



ICP-OES



ICP-MS





Altus Fluor Detektor



Altus UV Detektor



Altus PDA Detektor



Altus RI Detektor



Altus[®] UPLC[®]



Amel Engineered Solutions



Altus HPLC



Clarus[®] GC and GC/MS



Empower[®] 3

Single and Multi-Instrument Platform



TurboMatrix[®] ATD



TurboMatrix HS



SNFR[®] GC Diffactory Port



Altus SQ Detektor

Trennung

Detektion



NexION ICP-MS Detektor

Was ist HPLC – ICP-MS ?



A

Die Erweiterung eines ICP-MS um eine chromatographische Trennung?

B

Die Erweiterung einer HPLC um einen hochempfindlichen, sehr spezifischen, nicht ganz unbilligen Detektor?

HPLC – ICP-MS



APPLICATION NOTE

HPLC/ICP-MS

Authors:
Helmut Ernstberger
Ken Neubauer
PerkinElmer, Inc.
Shelton, CT

Accurate and Rapid Determination of Arsenic Speciation in Apple Juice

Introduction

In the past several years, concern about the presence of arsenic (As) in apple juice has grown greatly due to its publicity in the popular media.

Arsenic can enter apple juice either naturally through environmental uptake by the apple trees or anthropogenically through the use of pesticides and/or contamination during processing. Regardless of how it enters the juice, the

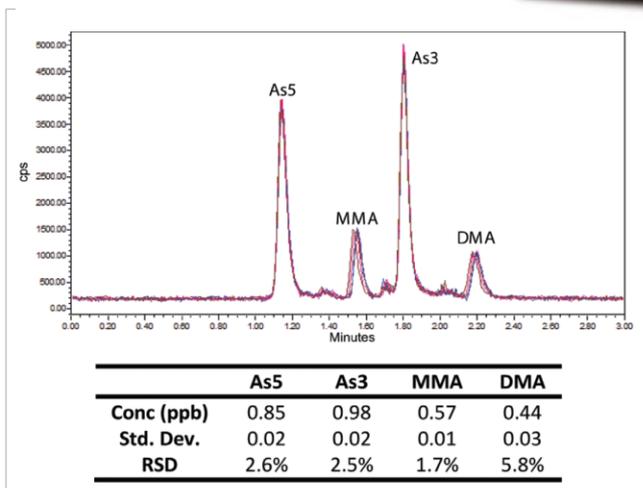


Figure 3. Overlay of seven consecutive injections of Apple Juice Sample 5, along with the associated concentrations and RSDs.

Table 1. Altus HPLC Conditions

Parameter	Condition
Column	C18, 4.6 x 250 mm, 5 µm
Mobile Phase	Octanesulfonic Acid (2 mM) + Malonic Acid (2 mM) + Methanol (1%)
pH	4.0 (adjusted with 10% NH ₄ OH)
Flow Rate	1.5 mL/min
Separation Scheme	Isocratic
Column Temperature	50 °C
Injection Volume	20 µL
LC Vials	Plastic, 1.5 mL

Table 2. NexION 350D ICP-MS Conditions

Parameter	Condition
Nebulizer	Glass Concentric
Spray Chamber	Glass Cyclonic
RF Power	1600 W
Nebulizer Flow	Optimized for < 2% oxides
Mode	Standard
Isotope	⁷⁵ As
Dwell Time	500 ms
Sampling Rate	2 points/second

HPLC – ICP-MS



91 AsO⁺
O₂

APPLICATION NOTE
HPLC/ICP-MS

Authors:
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75 As⁺
CH₄

APPLICATION NOTE
HPLC/ICP-MS

Authors:
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Inorganic Product Specialists
PerkinElmer Japan Co., Ltd.

Arsenic Speciation Analysis in White Rice by HPLC/ICP-MS

Introduction

There has been a rising concern about the presence of arsenic in rice, especially in societies which consume large quantities of rice. Arsenic can enter rice naturally through the environment or through the application of pesticides. Because not all arsenic species are toxic, the ability to measure the different forms is important.

Table 1. HPLC Conditions

Parameter	Condition
Instrument	Flexar HPLC System
Separation scheme	Isocratic
Flow rate	1.5 mL/min
Injection volume	50 µL
Column	C18
Column temperature	Room temperature

Table 2. ICP-MS Conditions

Parameter	Condition
Instrument	NexION 300D ICP-MS
Spray chamber	Glass cyclonic
Nebulizer	Glass concentric
Analyte monitored	AsO ⁺ (m/z 91)
Cell gas	O ₂ = 0.5 mL/min
RPq	0.45
Dwell time	500 ms

Arsenic Speciation Analysis in Brown Rice by HPLC/ICP-MS

Introduction

Arsenic (As) is a well-known toxic element which has been highly regulated, especially for drinking water. Although regulatory limits have been for total arsenic, its toxicity varies widely and is dependent on its chemical form. For example, inorganic forms of arsenic are highly toxic and carcinogenic. However, organic forms (such as monomethylarsonic acid, dimethylarsinic acid, and arsenobetaine) are recognized as non-toxic or as having low toxicity.

Table 1. HPLC Conditions

Parameter	Condition
Instrument	Flexar HPLC
Column	4.6 mm × 250 mm, 5 µm particles
Mobile phase	10 mmol/L 1-butanefulfonic acid (sodium salt) 4 mmol/L tetramethyl ammonium hydroxide, 4 mmol/L malonic acid, 0.05 % methanol, 0.03% nitric acid
Flow	0.8 mL/min
Column temperature	Room temperature
Injection volume	10 µL

Table 2. ICP-MS Conditions

Parameter	Condition
Instrument	NexION 300D ICP-MS
RF power	1600W
Analyte	m/z ⁷⁵ As
Cell conditions	Methane, 0.3 mL/min

HPLC – ICP-MS



APPLICATION NOTE

HPLC/ICP-MS

Authors:

Kenneth R. Neubauer

Pamela A. Perrone

Wilhad M. Reuter

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Shelton, CT 06484 USA

Advances in Bromine Speciation by HPLC/ICP-MS

Introduction

Bromine is a natural component found in waters, most commonly as the bromide ion, Br⁻. A common procedure for purifying drinking waters is treatment with ozone to kill bacteria. A byproduct of ozonolysis is the conversion of bromide to bromate (BrO₃⁻),

a known carcinogen. Therefore, a need exists to measure both bromide and bromate in drinking waters, as opposed to total bromine content.

Table 1. HPLC Isocratic Method Parameters.

HPLC System	PerkinElmer Series 200 Quaternary Pump, Autosampler, Vacuum Degasser, Peltier Column Oven
Column	ZirChrom®-SAX (3 µm, 100 x 4.6 mm)
Mobile Phase	18 mM NH ₄ OH + 3 mM HNO ₃
pH	10.2
pH Adjustment	None
Flow Rate	1.5 mL/min
Column Temperature	50 °C
Injection Volume	50 µL
Run Time	4 minutes
Total Analysis Time	4 minutes

Table 2. HPLC Gradient Method Parameters.

HPLC System	PerkinElmer Series 200 Quaternary Pump, Autosampler, Vacuum Degasser, Peltier Column Oven
Column	ZirChrom®-SAX (3 µm, 100 x 4.6 mm)
Solvent A	14 mM NH ₄ OH + 6 mM HNO ₃ ; pH=7.3
Solvent B	18 mM NH ₄ OH + 3 mM HNO ₃ ; pH=10.2
Gradient Profile	2 min at 100% A Step to 100% B 4 min at 100% B
Re-equilibration Time	5 min
pH Adjustment	None
Flow Rate	1.5 mL/min
Column Temperature	50 °C
Injection Volume	50 µL
Run Time	6 min
Total Analysis Time	11 min

Table 3. ICP-MS Conditions.

Instrument	PerkinElmer ELAN DRC II
Nebulizer	Quartz Concentric
Spray Chamber	Quartz Cyclonic
RF Power	1500 W
Dwell Time	250 ms
Analytes	Standard Mode – ⁷⁹ Br ⁺ DRC Mode – ^{79,81} BrO ⁺ (m/z 95, 97)
Reaction Gas	Standard Mode – None DRC Mode – N ₂ O = 0.5
RPq	Standard Mode – 0.25 DRC Mode – 0.50

UPLC – ICP-MS

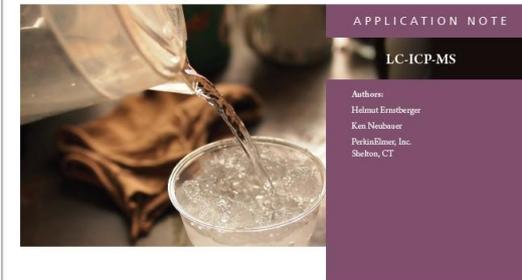
UPLC = Miniaturisierung
der Trenntechnik



Altus 30

Ultra Performance Chromatographie

- Geringe Volumina
- Wenig Lösemittel
- Kleinere Oberflächen
- Weniger Kontamination
- Weniger Memoryeffekt

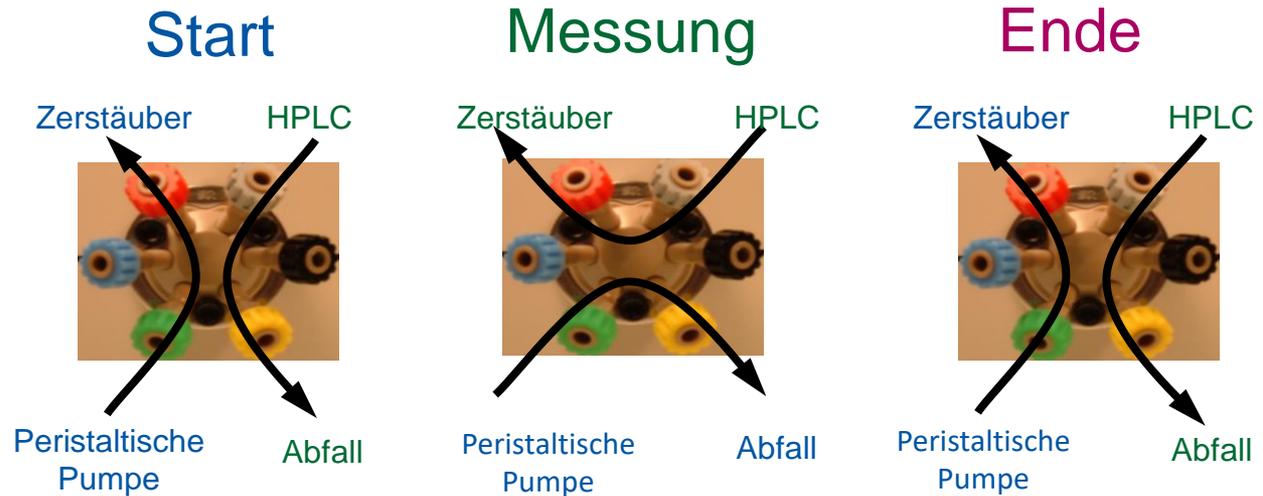


Chromium Speciation in Drinking Water by LC-ICP-MS

Introduction

With the growing concern of pollutants in the environment, more focus has been placed on identifying not only the total concentration of metals, but also the states in which they exist. Many elements can exist in various forms, either with different oxidation states or associated with various organic compounds or other elements. The toxicity and environmental impact of elements can vary depending in which form(s) they exist.

LC – ICP-MS: Automatisches Umschaltventil



- ICP-MS Analysen oder Tuning mit normalem Autosampler
- Säule wird parallel konditioniert

- Empower schaltet um, Chromatogramm startet
- Sauberer Labortisch

- Empower schaltet zurück
- Zerstäuber wird gespült, kein Eluent mehr auf die Konen
- Säule wird parallel konditioniert

GC – ICP-MS



APPLICATION NOTE

GC/ICP-MS

Authors:
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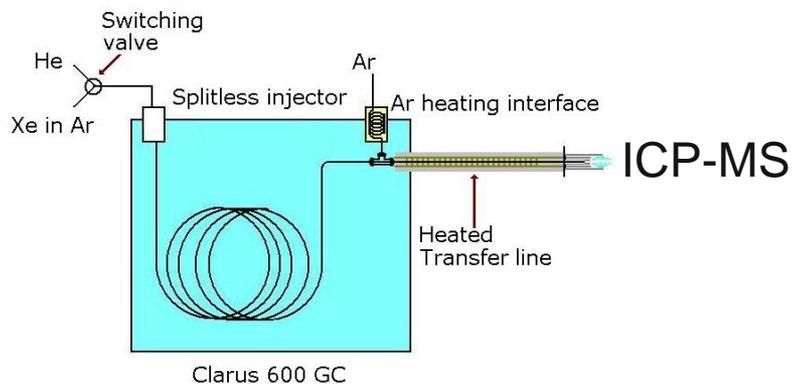
*PerkinElmer, Inc.
710 Bridgeport Avenue
Shelton, CT

Speciation of Organotin Compounds in Biological Tissues by GC/ICP-MS Using the NexION 3000/3500

Introduction

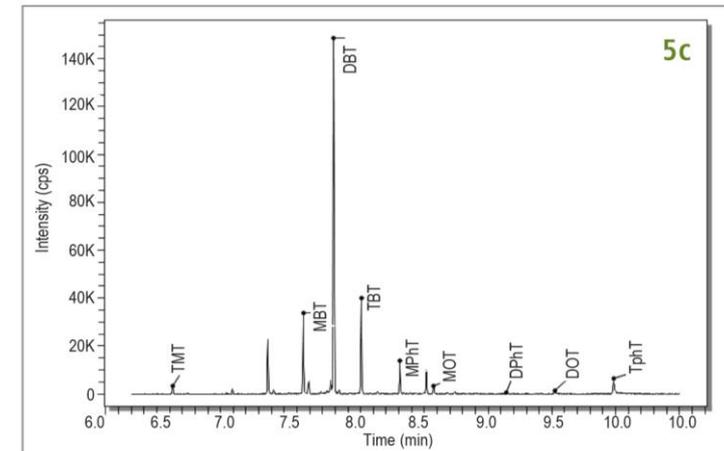
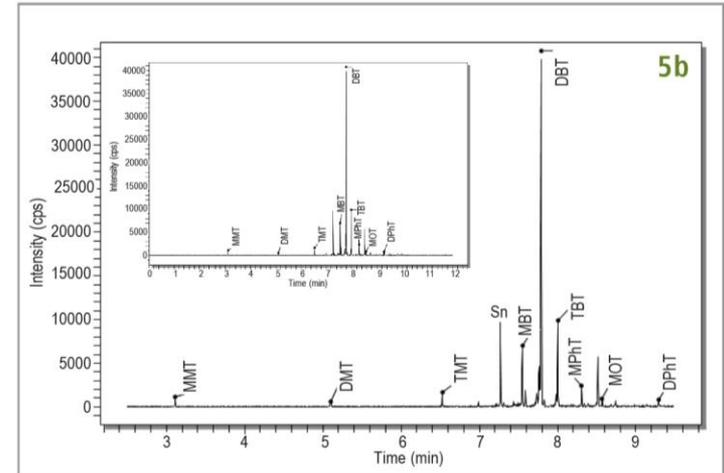
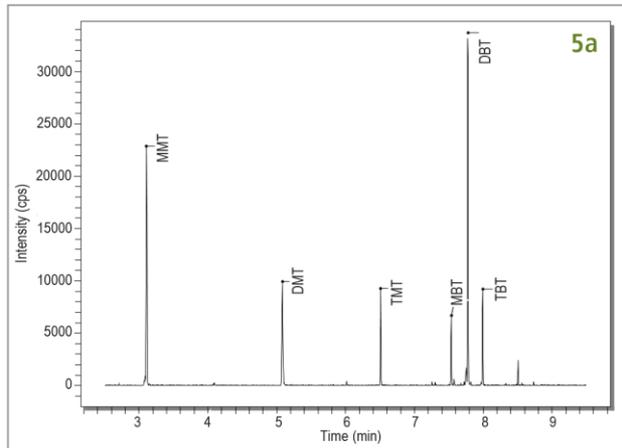
The environmental concerns regarding organotin compounds are of great importance due to their extensive use

for agricultural, industrial and domestic applications.¹ Butyl- and phenyl-tins



GC Parameters (Clarus 580)	Conditions
Column:	Elite-SMS (5%Diphenyl-dimethylpolysiloxane) (30 m, id 0.25 mm, d.f. 0.25 µm)
Injection port:	Splitless
Injection port temperature:	250 °C
Injection volume:	1.0 µL
He carrier gas flow (mL/min):	2.0
Transfer line temperature:	300 °C
Transfer line capillary:	Elite - Siltek deactivated fused-silica (id 0.25 mm)
Transfer line capillary position:	7 cm back from tip of Silcosteel® tube
Oven program:	50 °C → ramp 10 °C/min → 100 °C → ramp 45 °C/min → 290 °C (3 min)
ICP-MS Parameters (NexION 300)	Conditions
RF power:	1600 W
Nebulizer flow rate:	0.90 L/min
Auxiliary gas flow rate:	1.2 L/min
Plasma gas flow rate:	15 L/min
Oxygen gas flow rate:	0.025 L/min
Injector diameter:	1.2 mm i.d.
Isotope/dwell times:	Sn: 118, 119, 120 (30 ms) N: 15 (30 ms)

GC – ICP-MS



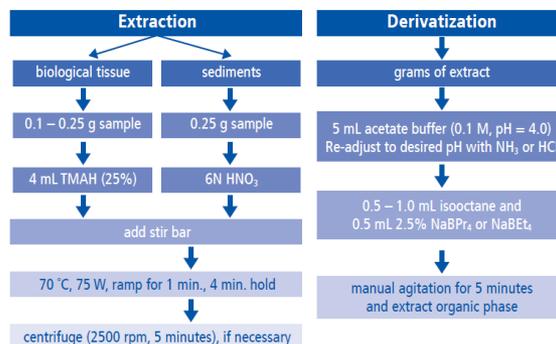
Figures 5a-5c. Chromatographic separation for the organotin species (^{120}Sn isotope) for a 0.25 ng/mL standard in isoctane (5a), oyster tissue (5b), and mussel tissue reference material (5c).

GC – ICP-MS



Table 1. GC/ICP-MS operating conditions.

GC Parameters (Clarus)	Conditions
Column:	Elite-SMS (5% Diphenyldimethylpolysiloxane) (30 m, i.d. 0.25 mm, d.f. 0.25 µm)
Injection port:	Splitless
Injection port temperature:	250 °C
Injection volume:	1.0 µL
He carrier gas flow (mL/min):	2.0
Transfer line temperature:	300 °C
Transfer line capillary:	Elite – Siltek deactivated fused-silica (i.d. 0.25 mm)
Oven program:	50 °C → ramp 10 °C/min → 100 °C → ramp 45 °C/min → 290 °C (3 min)
ICP-MS Parameters (NexION)	Conditions
RF power (W):	1600 W
Nebulizer flow rate (L/min):	0.98
Auxiliary gas flow rate (L/min):	1.2
Plasma gas flow rate (L/min):	15
Oxygen gas flow rate (L/min):	0.025
Injector diameter:	1.2 mm i.d.
Isotope/dwell times:	Hg: 199, 201, 202; N: 15 (30 ms)



APPLICATION NOTE

GC/ICP - MS

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 PerkinElmer, Inc.
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Mercury Speciation in Biological Tissue and Sediments by GC/ICP-MS Using the NexION 300D/350D

Introduction

The chemical determination of mercury (Hg) species in the environment is gaining increasing interest both for improved understanding of their reactional pathways and also to meet regulation limits in both Europe and the U.S. Mercury species play an important role in environmental pollution because they can result from anthropogenic activities, as well as natural biomethylation processes.¹

Table 3. Concentration results for MMHg (expressed ng/g as ²⁰²Hg) obtained in the analysis of various reference materials (n=3).

Reference Materials	Certified Values	Experimental Values	%RSD	Recovery (%)
BCR 464 (tuna fish)	5500 ±170	4505 ±98	2.2	82
BCR (oyster tissue)	107 ±17	104 ±7	6.7	97
IAEA 405 (estuarine sediment)	5.49 ±0.53	5.41 ±0.34	6.3	99

Wie gelangen die heißen Gase vom GC in das Plasma?

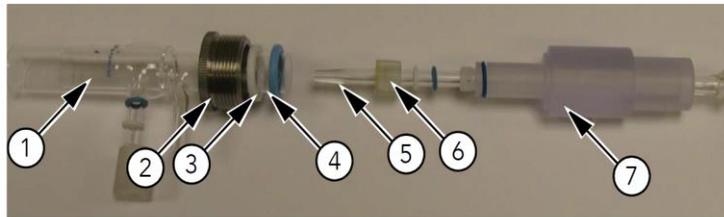
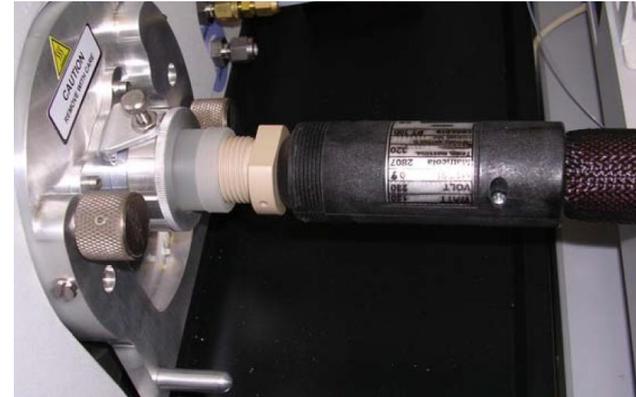
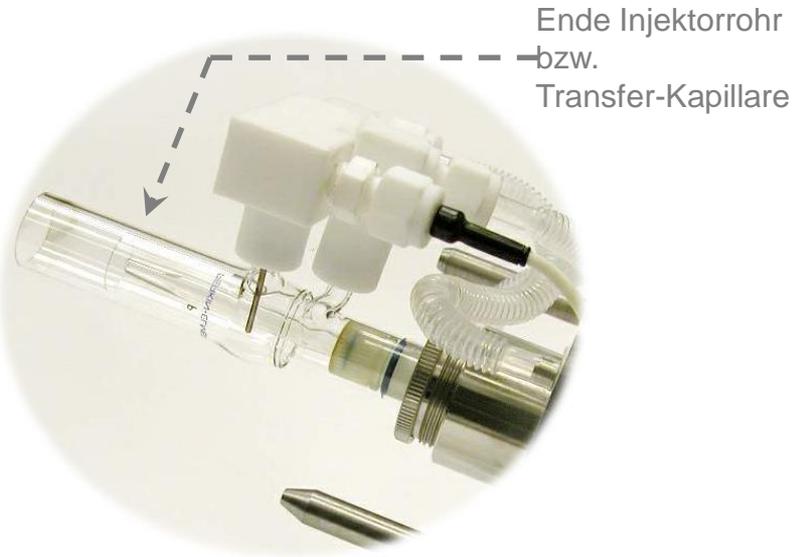


Abb. 3-32. Einzelteile der ICP-Fackel und des Injektoradapters

Nr.	Beschreibung	Nr.	Beschreibung
1	Quarzfackel	5	Injektor
2	Interne Z-Justagemutter	6	Injektormutter
3	Teflondistanzring	7	Fackeladapter
4	Blauer O-Ring		

- Transfer-Kapillare vom GC hat am ICP-MS die Form von Fackel-Adapter mit Injektor
- Ende der Kapillare entspricht dem Ende des Injektorrohres
- Nur Fackel aufstecken und mit Schnellwechsel-Bajonett verschrauben
- Gase vom GC in einen vorgeheizten Argonstrom geleitet
- Diese Make-up Argon liefert der MFC für das Zerstäubergas des ICP-MS

Wie gelangen die heißen Gase vom GC in das Plasma?

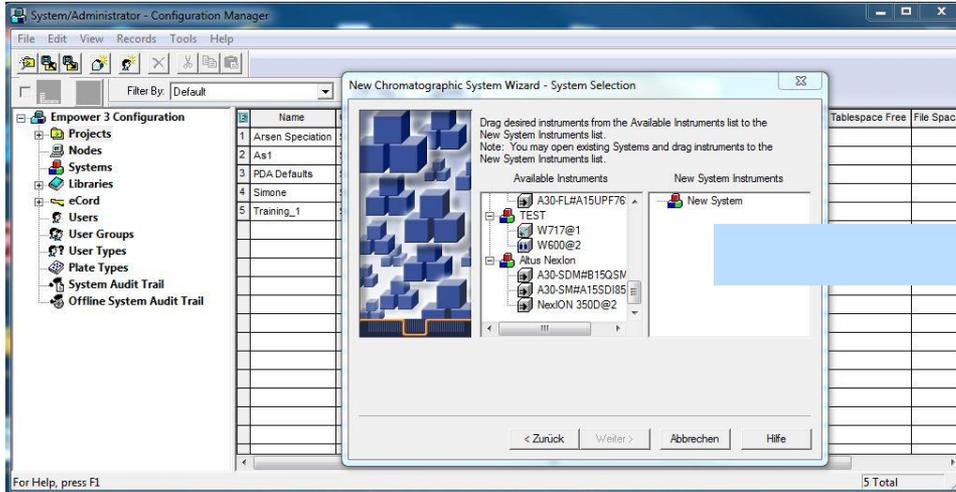


15 Wir reden hier von 300°C, "beheizte" Kapillare ist etwas untertrieben!



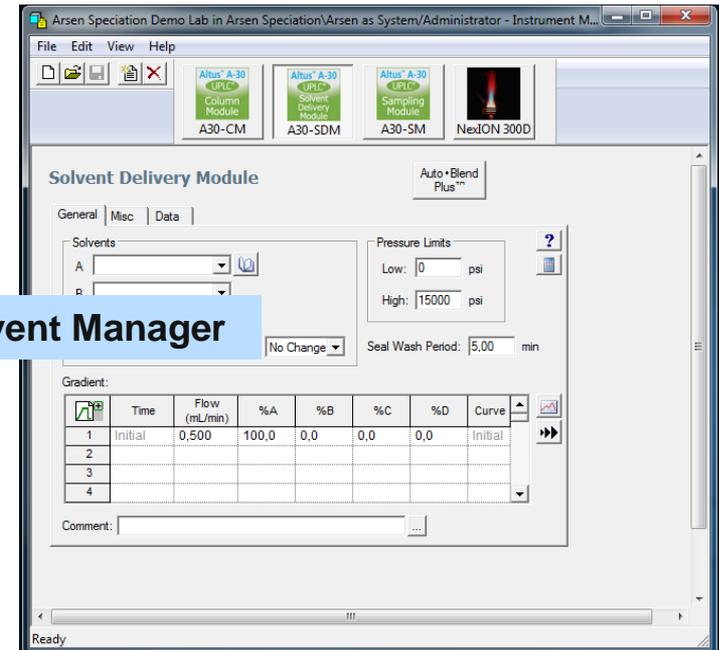
Professionelle Chromatographie Datenverarbeitung

Konfigurieren Sie sich Ihren Messplatz



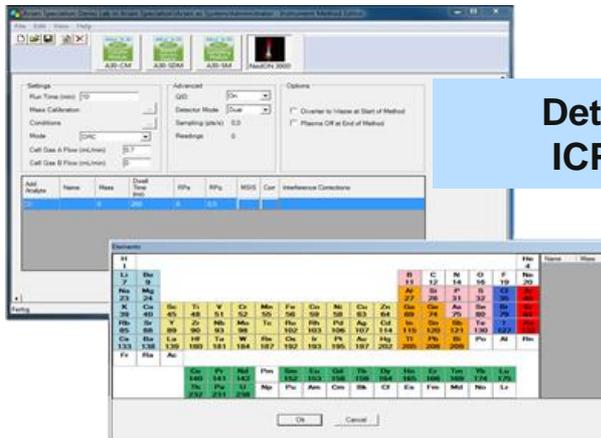
Schaltfläche für Komponenten erstellen

1. Solvent Manager
2. Säulenofen
3. LC Autosampler
4. Detektoren



Detektor ICP-MS

Solvent Manager



NextION8000 in Speciation as System/Administrator - QuickStart - [Run Samples]

File Edit View Inject Actions Customize Manage Help

Run Only Continue on Fault Apply Table Preferences Sample Set Method

Sample Set Method: Cr_Speciation.mil.Kalibration

#	Vial	Inj Vol (uL)	# of Injs	Label	SampleName	Level	Function	Method Set / Report Method	Label Reference	Processing	Run Time (Minutes)	Data Start (Minutes)	Next Inj. Delay (Minutes)	MS Tune Method	MS Calibration Method	Column Position	Auto Additions	SampleWeight	Dilution
1							Clear Calibration	Cr_Spez Iso_Std		Normal									
2	9	30.0	1	S0101	Std	1	Inject Standards	Cr_Spez Iso_Std		Normal	4.00	0.00	0.00					1.00000	1.00000
3	10	30.0	1	S0102	Std	2	Inject Standards	Cr_Spez Iso_Std		Normal	4.00	0.00	0.00					1.00000	1.00000
4	11	30.0	1	S0103	Std	5	Inject Standards	Cr_Spez Iso_Std		Normal	4.00	0.00	0.00					1.00000	1.00000
5	4	30.0	1	U0101	Eluent		Inject Samples	Cr_Spez Iso_Std		Normal	4.00	0.00	0.00					1.00000	1.00000
6	1	30.0	1	U0102	Cr-Mix		Inject Samples	Cr_Spez Iso_Std		Normal	4.00	0.00	0.00					1.00000	1.00000
7	2	30.0	1	U0103	Cr-3		Inject Samples	Cr_Spez Iso_Std		Normal	4.00	0.00	0.00					1.00000	1.00000
8	3	30.0	1	U0104	Cr-6		Inject Samples	Cr_Spez Iso_Std		Normal	4.00	0.00	0.00					1.00000	1.00000

Sample Set

NextION ICP-MS

Instrument: Idle

Vacuum Pressure: 1E-06 Torr

Nebulizer Gas Flow: 0.81 L/min

ICP RF Power: 1603 W

Lens Voltage: -10 V

Main Water Temp: 19.587 °C

Interface Water Temp: 43.304 °C

Plasma: ON

Secondary Gas: ON

Argon Pressure: OK

Plasma Gas: OK

Torch Box Temp: 48.054 °C

Sample Set Time Remaining: 0:00:00:00

Total Samples Time Remaining: 0:00:00:00

New Sample Set Time: 0:00:37:45

Sample Set

Solvent Delivery Module: Flow 0.000 mL/min

Column Module: Column Selection Column 2, Temperature 30.0 °C

Sampling Module: Sample 10.2 °C, 10.0

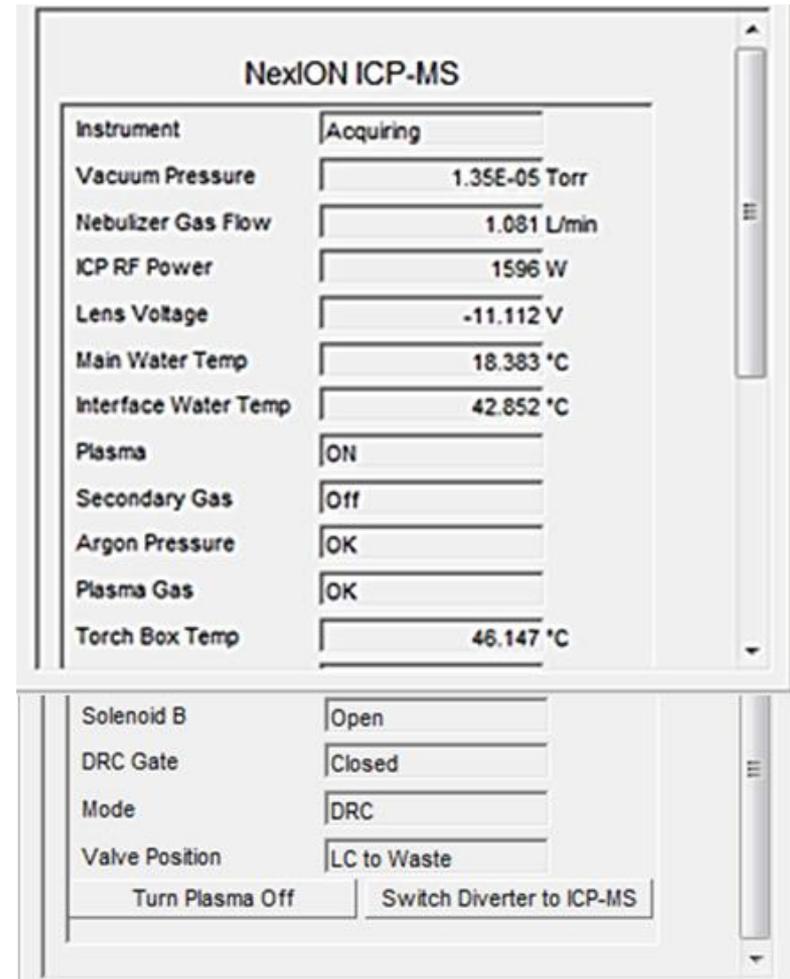
HPLC/UPLC Control Panel

Überwacht NexION Status in Echtzeit

- Vakuum
- Generatorleistung
- Zerstäubergas
- QID
- Kühlwasser
- Zellmodus

Schaltflächen für:

- Plasma An/Aus
- Schaltventil (Diverter)

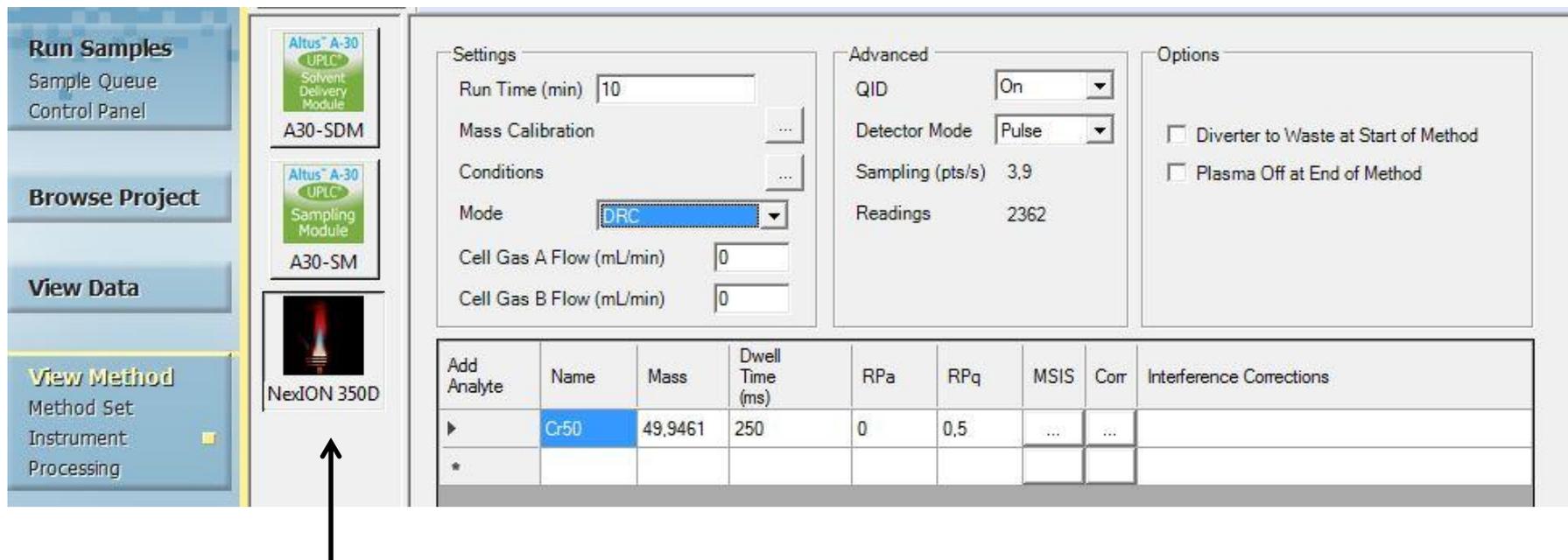


NexION ICP-MS

Instrument	Acquiring
Vacuum Pressure	1.35E-05 Torr
Nebulizer Gas Flow	1.081 L/min
ICP RF Power	1596 W
Lens Voltage	-11.112 V
Main Water Temp	18.383 °C
Interface Water Temp	42.852 °C
Plasma	ON
Secondary Gas	Off
Argon Pressure	OK
Plasma Gas	OK
Torch Box Temp	46.147 °C

Solenoid B	Open
DRC Gate	Closed
Mode	DRC
Valve Position	LC to Waste

Turn Plasma Off Switch Diverter to ICP-MS



Settings

Run Time (min) 10

Mass Calibration ...

Conditions ...

Mode **DRC**

Cell Gas A Flow (mL/min) 0

Cell Gas B Flow (mL/min) 0

Advanced

QID On

Detector Mode Pulse

Sampling (pts/s) 3,9

Readings 2362

Options

Diverter to Waste at Start of Method

Plasma Off at End of Method

Add Analyte	Name	Mass	Dwell Time (ms)	RPa	RPq	MSIS	Corr	Interference Corrections
▶	Cr-50	49,9461	250	0	0,5	
*								

**Schaltfläche
NexION**

... und los geht's

Run Samples

Sample Queue
Control Panel

Browse Project

View Data

View Method

Method Set
Instrument
Processing

Show Me...

Altus A-30 UPLC Solvent Delivery Module
A30-SDM

Altus A-30 UPLC Sampling Module
A30-SM



NexION 350D

Settings

Run Time (min)

Mass Calibration C:\U...\Default.tun ...

Conditions C:\U...\Default.dac ...

Mode

Cell Gas A Flow (mL/min)

Cell Gas B Flow (mL/min)

Advanced

QID

Detector Mode

Sampling (pts/s) 1.3

Readings 787

Options

Diverter to Waste at Start of Method

Plasma Off at End of Method

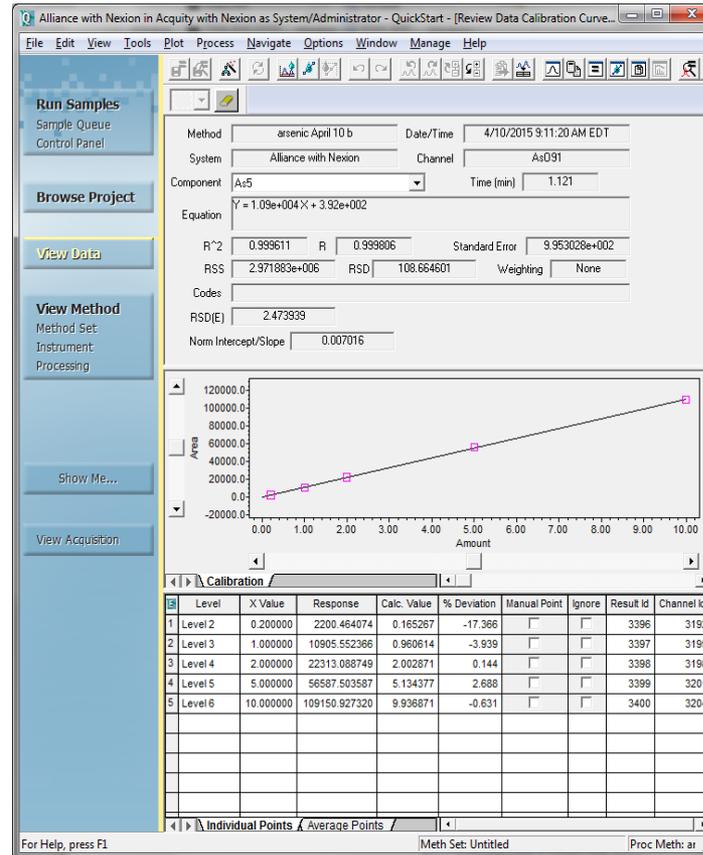
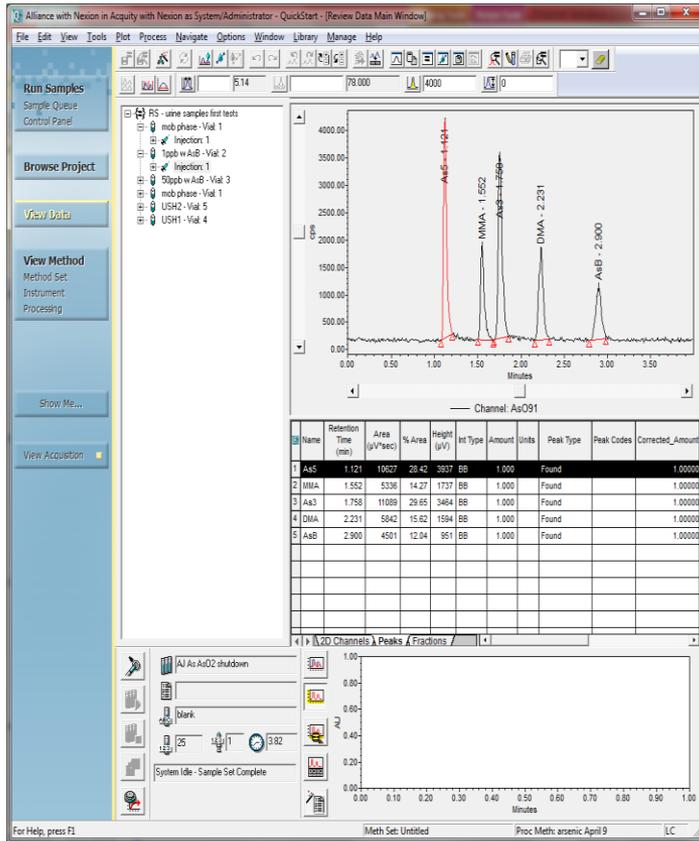
Add Analyte	Name	Mass	Dwell Time (ms)	RPa	RPq	MSIS	Corr	Interference Corrections
▶	Cr50	49,9461	250	0	0.5	
	As75	74,9216	250	0	0.5	
	Se78	77,9173	250	0	0.5	

Elements

																		H											He	Name	Mass								
																		1											4										
Li		Be																B		C		N		O		F		Ne											
7		9																11		12		14		16		19		20											
Na		Mg																27		28		31		32		35		40											
23		24		K		Ca		Sc		Ti		V		Cr		Mn		Fe		Co		Ni		Cu		Zn		Ga		Ge		As		Se		Br		Kr	
39		40		45		48		51		52		55		56		59		58		63		64		69		74		75		80		79		84					
Rb		Sr		Y		Zr		Nb		Mo		Tc		Ru		Rh		Pd		Ag		Cd		In		Sn		Sb		Te		I		Xe					
85		88		89		90		93		98		102		103		106		107		114		115		120		121		130		127		132							
Cs		Ba		La		Hf		Ta		W		Re		Os		Ir		Pt		Au		Hg		Tl		Pb		Bi		Po		At		Rn					
133		138		139		180		181		184		187		192		193		195		197		202		205		208		209											
Fr		Ra		Ac																																			

Ok Cancel

- Auswahl mehrerer Massen/Isotope möglich
- Zelleinstellungen
- Massenkalibration und Bedingungen können geladen werden
- Plasma „Aus“ am Ende des Laufs
- Schaltventil



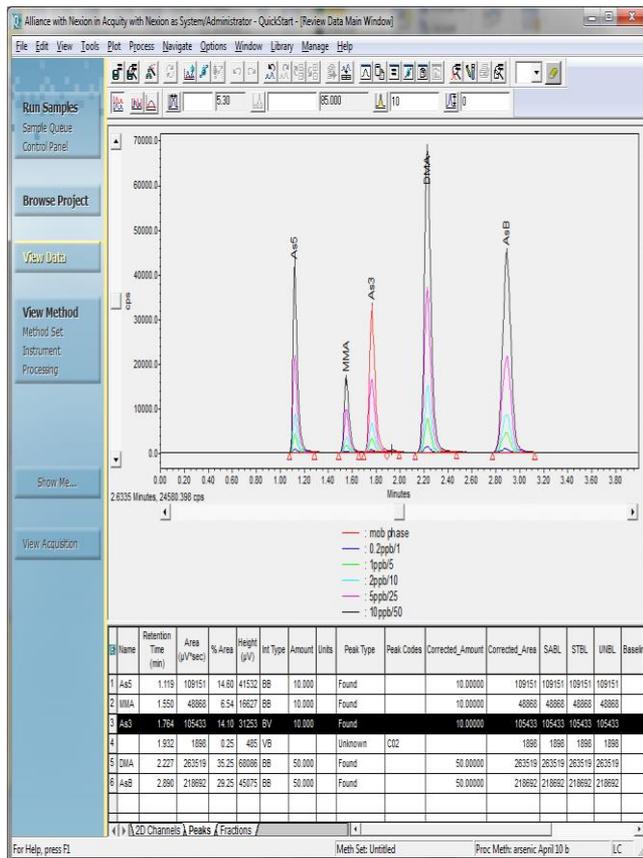
Regression

Kalibrierkurve

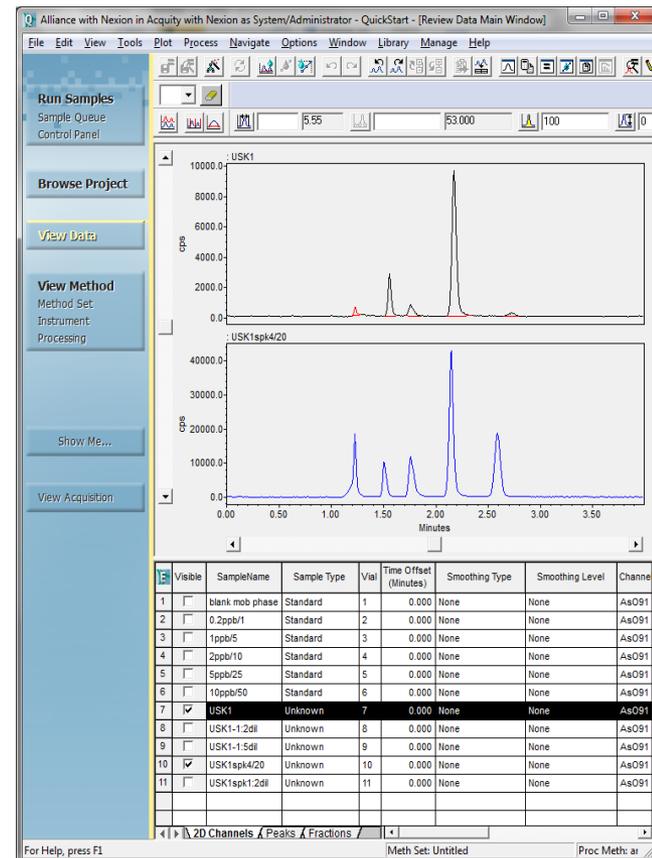
Details

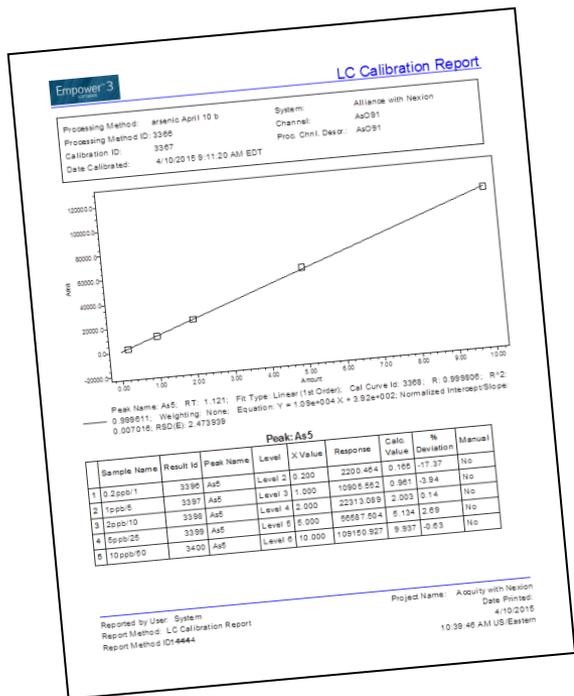
Peakflächen & manuelle Integration

Overlay verschiedener Chromatogramme



Stapelansicht verschiedener Chromatogramme





Empower 3 Component Summary

Component Summary For Retention Time

Channel: As091

Sample Name	Inj	Channel	Val	As5	MMA	As3	DMA	AsB	
1	USK1	1	As091	7	1.231	1.549	1.757	2.170	2.732
2	USK1ppb420	1	As091	8	1.228	1.513	1.759	2.144	2.593
3	USHQppb420	1	As091	9	1.290	1.562	1.762	2.178	2.737
4	USHC	1	As091	10	1.353	1.524	1.759	2.150	2.607
Mean				1.304	1.536	1.759	2.162	2.687	
Std. Dev.				0.047	0.018	0.002	0.010	0.091	
% RSD				3.3	1.2	0.1	0.1	3.0	

Component Summary For Area

Channel: As091

Sample Name	Inj	Channel	Val	As5	MMA	As3	DMA	AsB	
1	USK1	1	As091	7	1910	6981	3189	33220	1168
2	USK1ppb420	1	As091	8	47049	28972	47892	144751	59997
3	USHQppb420	1	As091	9	48670	28248	47395	137652	221931
4	USHC	1	As091	10	2472	8928	4934	29398	130414
Mean				25221	17732	25499	89313	111281	
Std. Dev.				28739	11937	26234	63934	91821	
% RSD				105.6	69.7	99.0	79.7	82.5	

Component Summary For Amount

Channel: As091

Sample Name	Inj	Channel	Val	As5	MMA	As3	DMA	AsB	
1	USK1	1	As091	7	0.139	0.321	0.290	0.999	0.168
2	USK1ppb420	1	As091	8	4.263	3.368	4.485	27.100	30.352
3	USHQppb420	1	As091	9	4.621	3.007	4.439	25.894	30.601
4	USHC	1	As091	10	0.180	0.249	0.332	0.243	30.171
Mean				2.278	3.388	2.401	18.030	28.332	
Std. Dev.				2.442	2.428	3.351	12.053	20.665	
% RSD				107.2	71.7	99.1	79.2	72.8	

Reported by User: System
Report Method: Component Summary
Report Method ID: 4441

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