Speciation ICP-MS

Altus LC, Clarus GC, NexION, Empower

Simone Korstian

Analytica 2016

PerkinElmer


Altus Fluo Detektor
Altus UV Detektor
Altus PDA Detektor
Altus RI Detektor
Amel Engineered Solutions
Altus™ UPLC®
Altus HPLC
Altus SQ Detektor
Clarus® GC and GC/MS
Empower® 3
Single and Multi-Instrument Platform
Trennung
Detektion
TurboMatrix™ ATD
TurboMatrix HS
SNIFF® GC Olfactory Port
NexION ICP-MS Detektor

Haben Sie bereits ein gutes Chromatographie System?

Alle wichtigen HPLC Anlagen

Alle wichtigen GC Anlagen

Agilent – Beckmann CE -- CTC Analytics -- DANI -- Dionex – Hitachi -- PE -- Shimadzu – Waters

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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?

Einkäufer: „A“ Analytiker: …?

HPLC – ICP-MS

APPLICATION NOTE

HPLC/ICP-MS

Authors:

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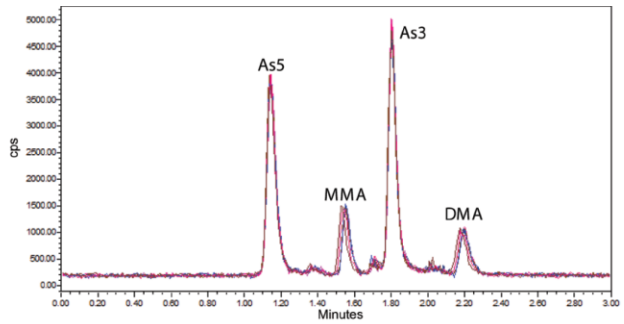
Shelton, CT

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



	As5	As3	MMA	DMA
Conc (ppb)	0.85	0.98	0.57	0.44
Std. Dev.	0.02	0.02	0.01	0.03
RSD	2.6%	2.5%	1.7%	5.8%

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_4OH)
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

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	O2 = 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-butanesulfonic 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

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HPLC – ICP-MS

APPLICATION NOTE

HPLC/ICP-MS

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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 (BrO_3^-), 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_4OH + 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_4OH + 6 mM HNO_3; pH=7.3
Solvent B	18 mM NH_4OH + 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_2O = 0.5
RPq	Standard Mode – 0.25 DRC Mode – 0.50

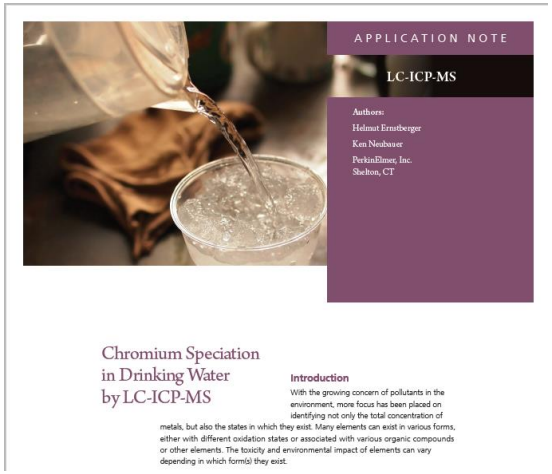
UPLC – ICP-MS

UPLC = Miniaturisierung
der Trenntechnik

Altus 30

Ultra Performance Chromatographie

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



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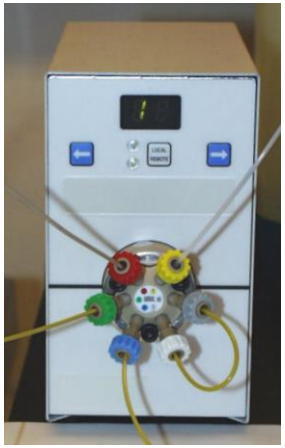
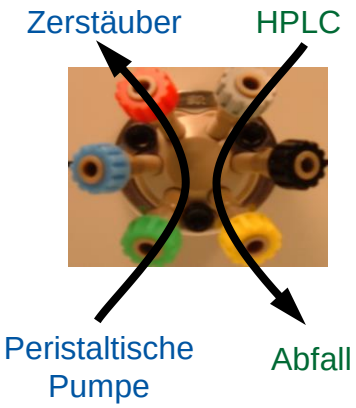
LC – ICP-MS: Automatisches Umschaltventil

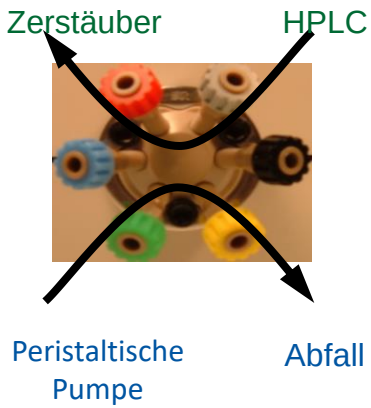


Start



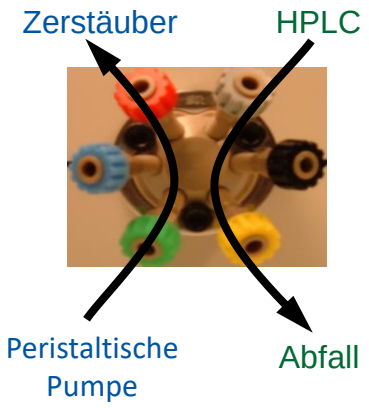
- ICP-MS Analysen oder Tuning mit normalem Autosampler
- Säule wird parallel konditioniert

Messung



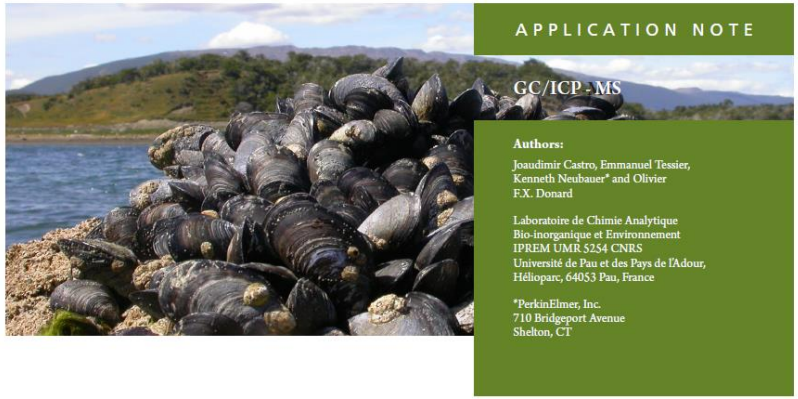
- Empower schaltet um, Chromatogramm startet
- Sauberer Labortisch

Ende



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

GC – ICP-MS



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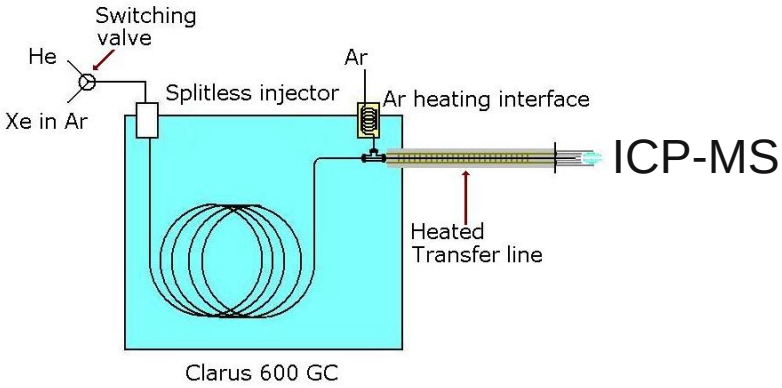
Speciation of Organotin Compounds in Biological Tissues by GC/ICP-MS Using the NexION 300D/350D

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-5MS (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)

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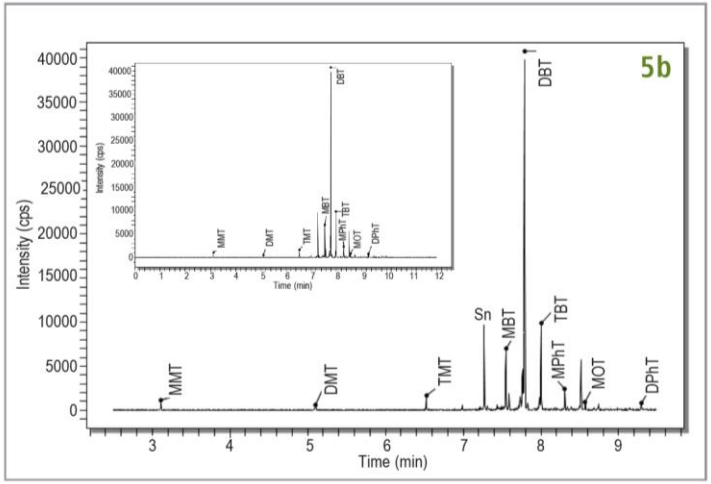
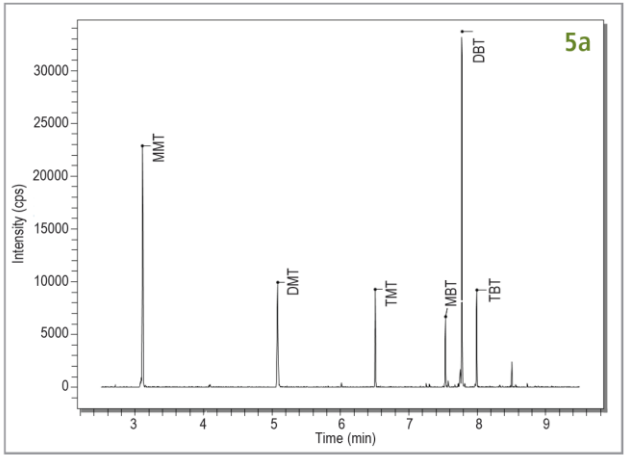
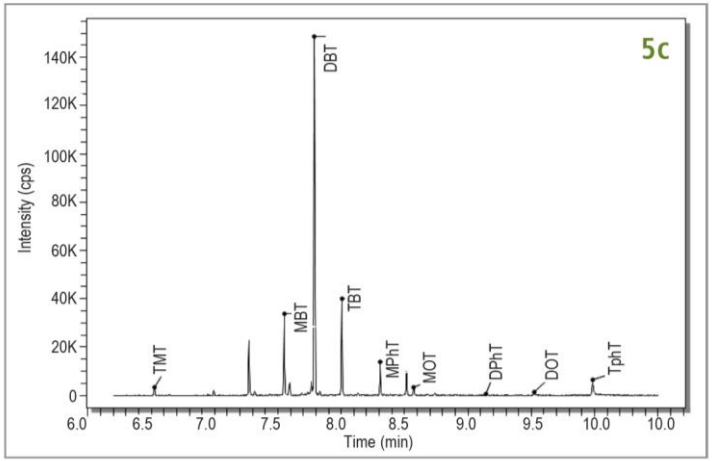
GC – ICP-MS







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

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GC – ICP-MS

APPLICATION NOTE

GC/ICP - MS

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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 1. **GC/ICP-MS operating conditions.**

GC Parameters (Clarus)	Conditions
Column:	Elite-5MS (5% Diphenyl-dimethylpolysiloxane) (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)

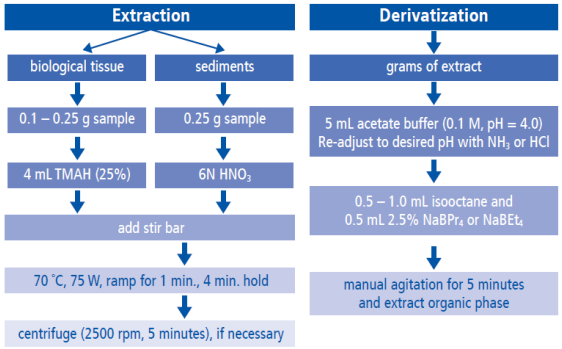

Table 3. Concentration results for MMHg (expressed ng/g as ^{202}Hg) obtained in the analysis of various reference materials (n=3).

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

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Wie gelangen die heißen Gase vom GC in das Plasma?

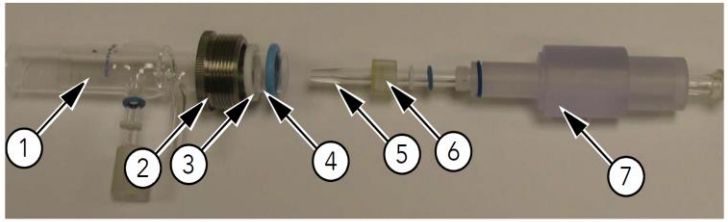


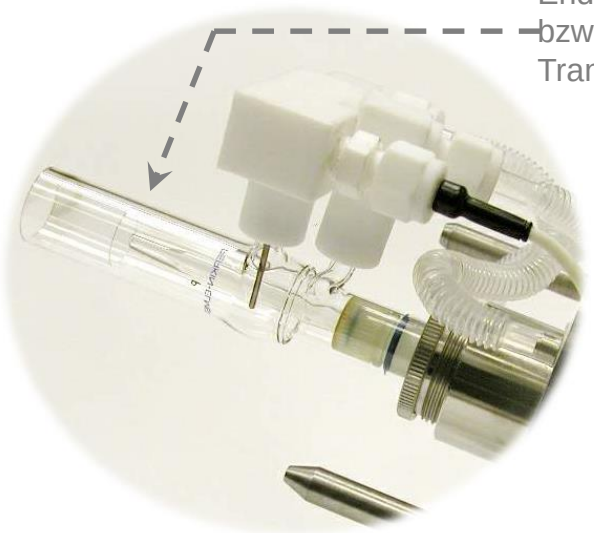
Abb. 3-32. Einzelteile der ICP-Fackel und des Injektoradapters

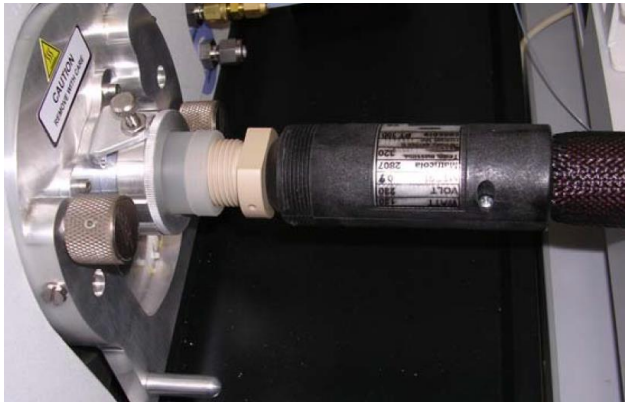
Nr.	Beschreibung	Nr.	Beschreibung
1	Quarzfackel	5	Injektor
2	Interne Z-Justagemutter	6	Injektormutter
3	Teflondistanzring	7	Fackeladapter
4	Blauer O-Ring		

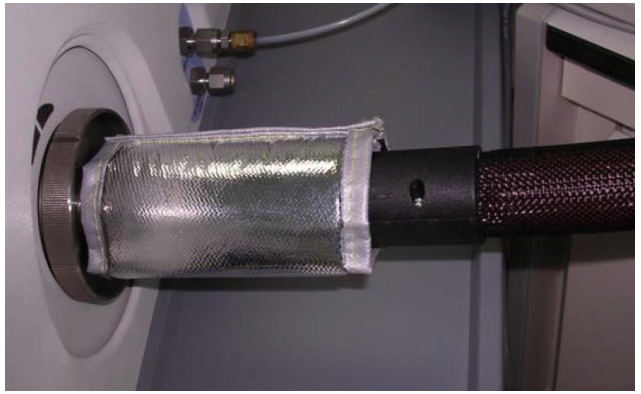
- Transfer-Kapillare vom GC hat am ICP-MS die Form von Fackel-Adapter mit Injektor
- Ende der Kapillare entspricht dem Ende des Injektorrohres
- Nur Fackel aufstecken und mit Schnellwechsel-Bajonett verschrauben

- 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?







Wir reden hier von 300°C, “beheizte” Kapillare ist etwas untertrieben!

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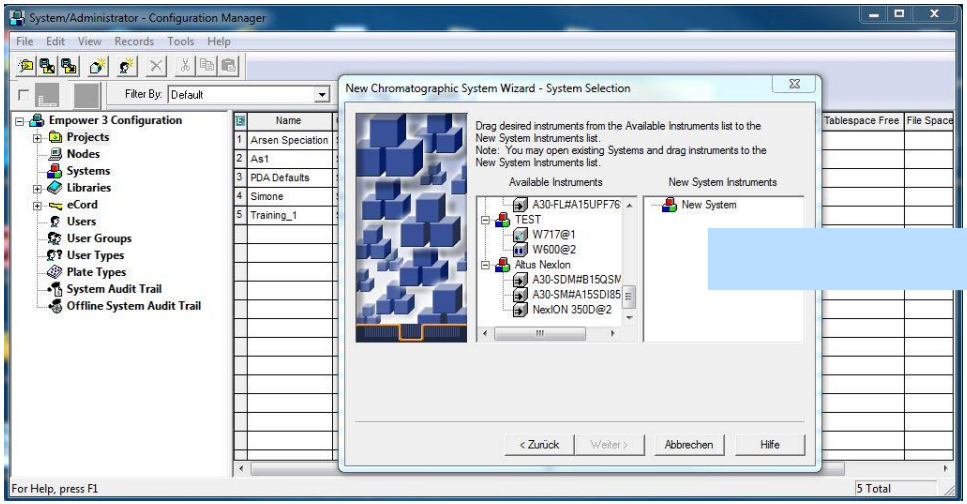
Professionelle Chromatographie Datenverarbeitung

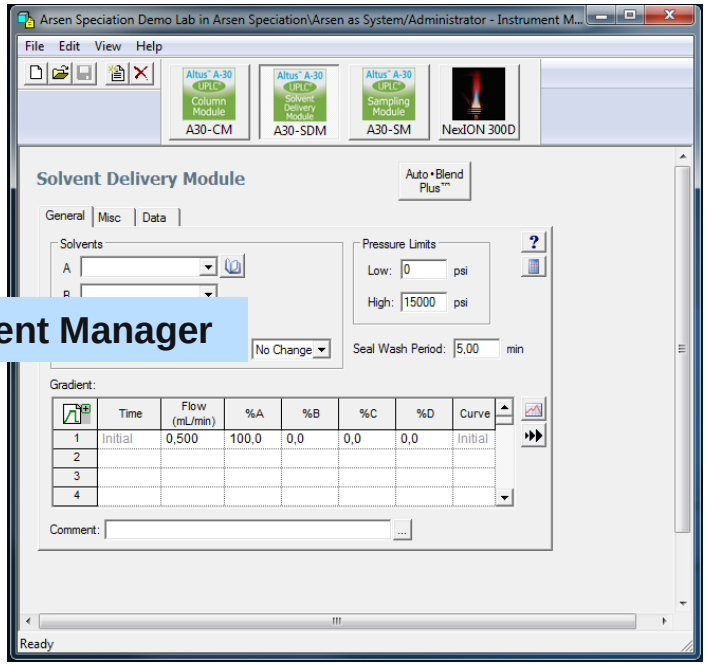
PerkinElmer

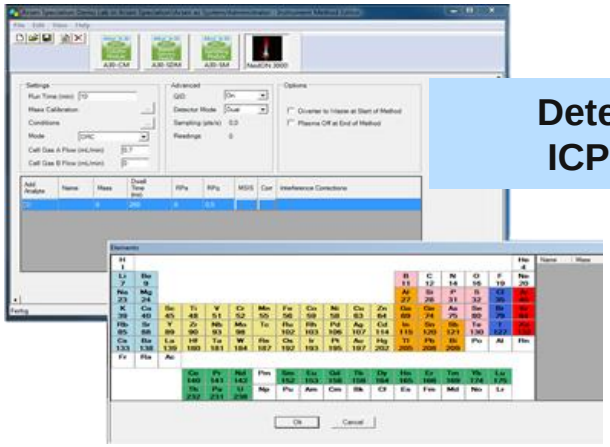
Konfigurieren Sie sich Ihren Messplatz



Schaltfläche für Komponenten erstellen

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

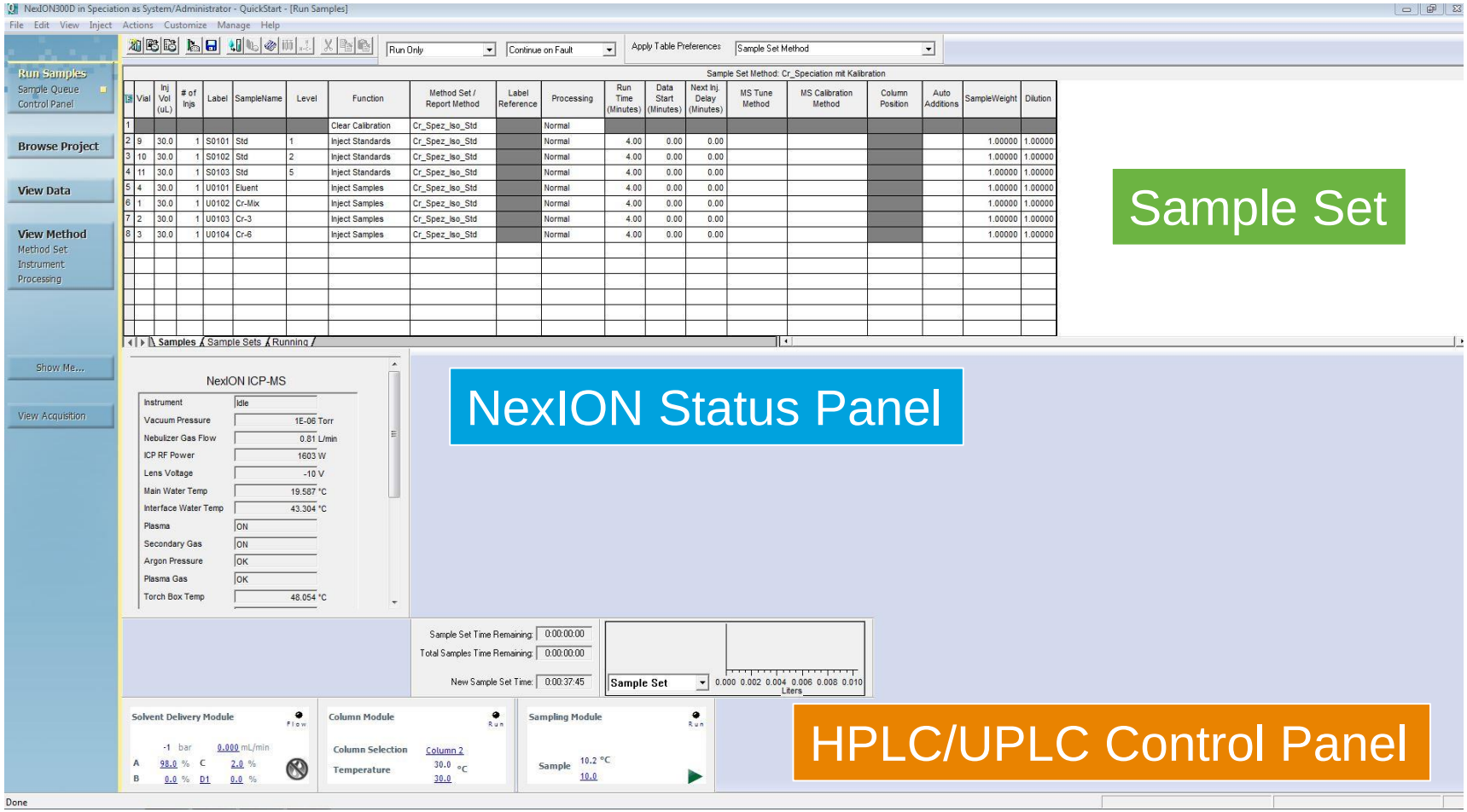




Detektor ICP-MS

Solvent Manager

Quickstart Interface



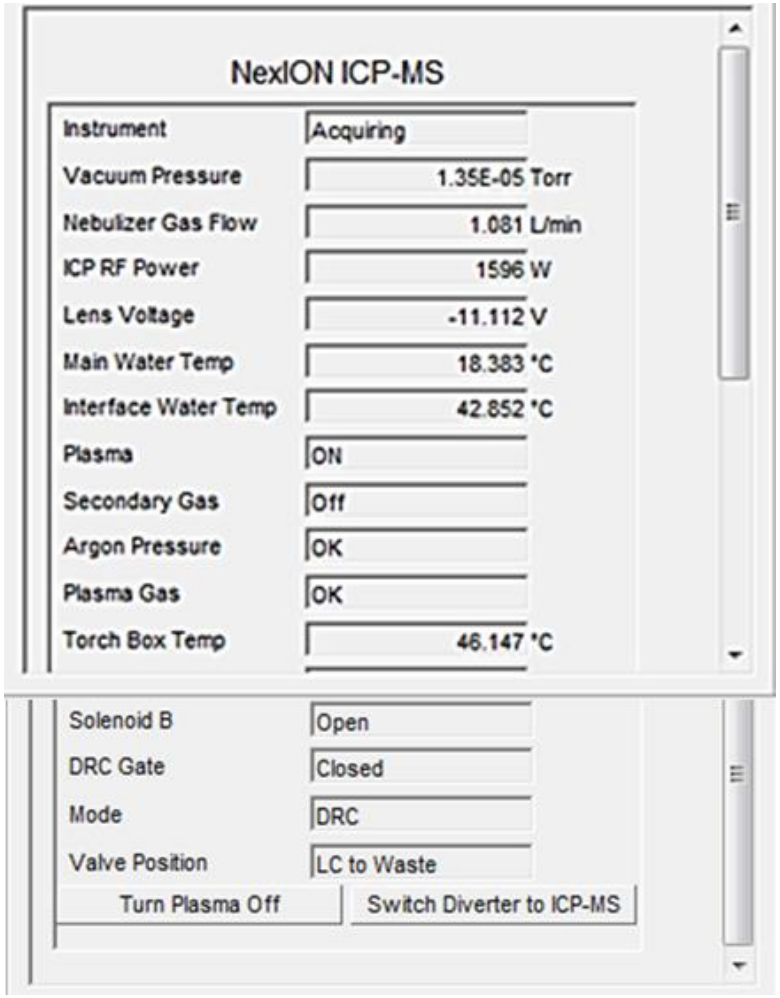
NexION Status-Fenster während der Datenaufnahme

Überwacht NexION Status in Echtzeit

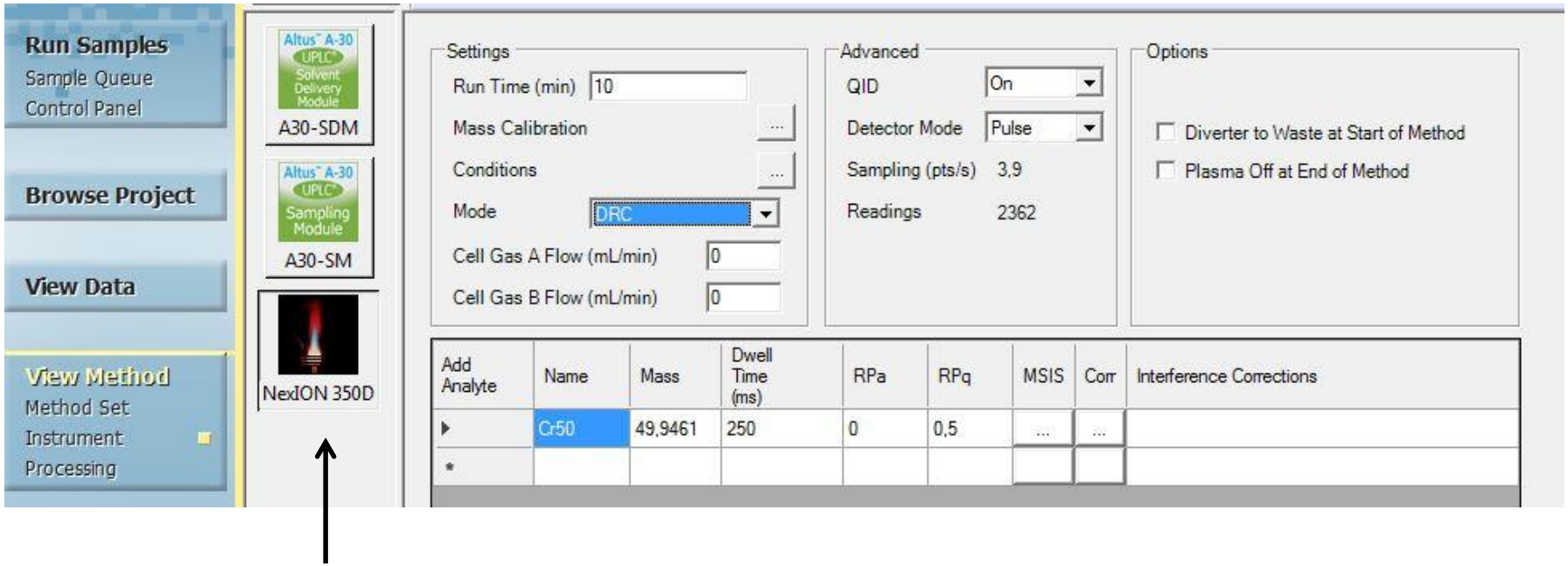
- Vakuum
- Generatorleistung
- Zerstäubergas
- QID
- Kühlwasser
- Zellmodus

Schaltflächen für:

- Plasma An/Aus
- Schaltventil (Diverter)



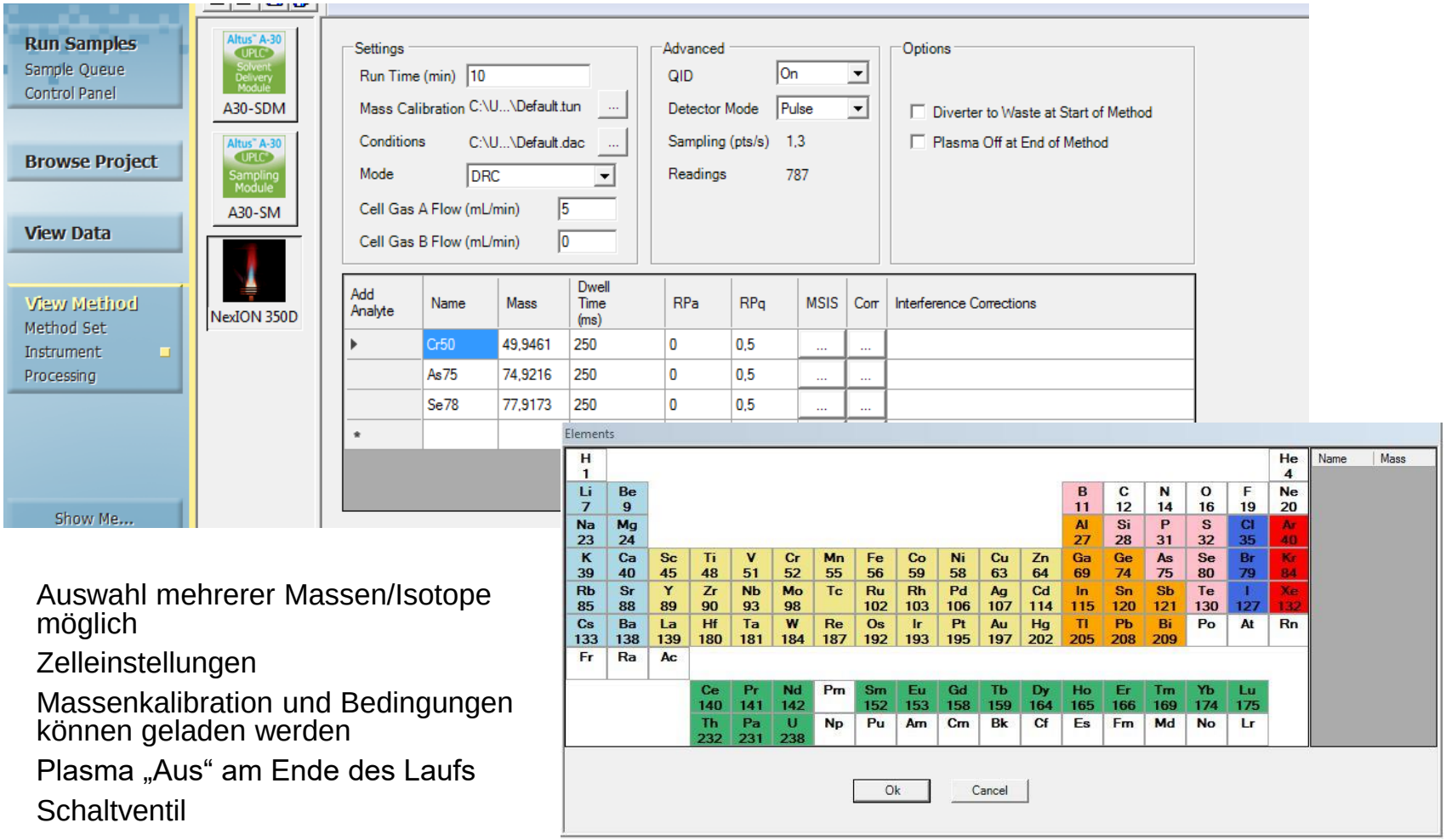
Steuerung des Detektors NexION



Schaltfäche NexION

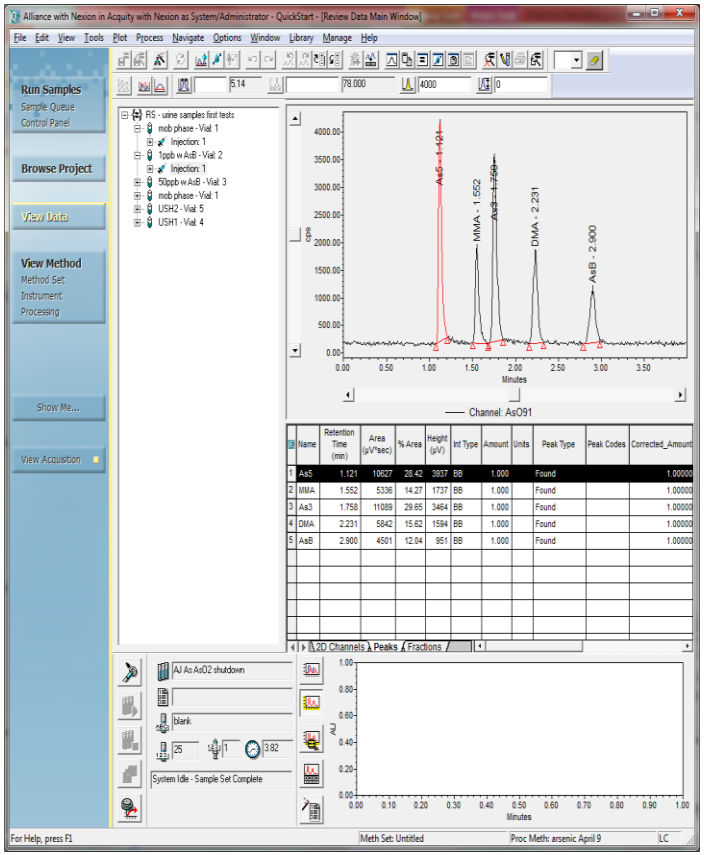
… und los geht’s

Steuerung des Detektors NexION

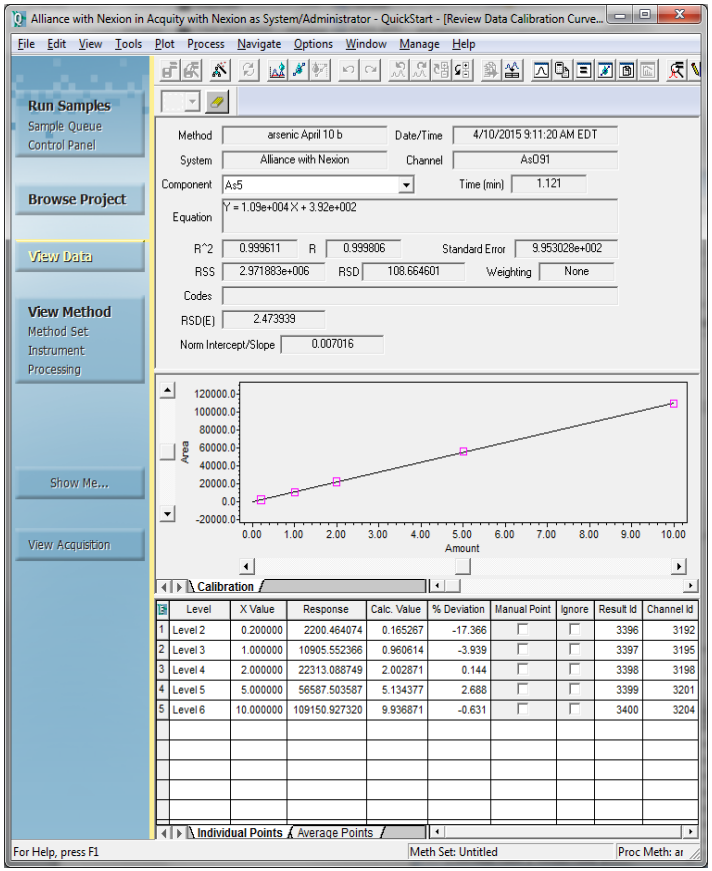


- Auswahl mehrerer Massen/Isotope möglich
- Zelleinstellungen
- Massenkalibration und Bedingungen können geladen werden
- Plasma „Aus“ am Ende des Laufs
- Schaltventil

Empower® 3



Peakflächen & manuelle Integration



Regression

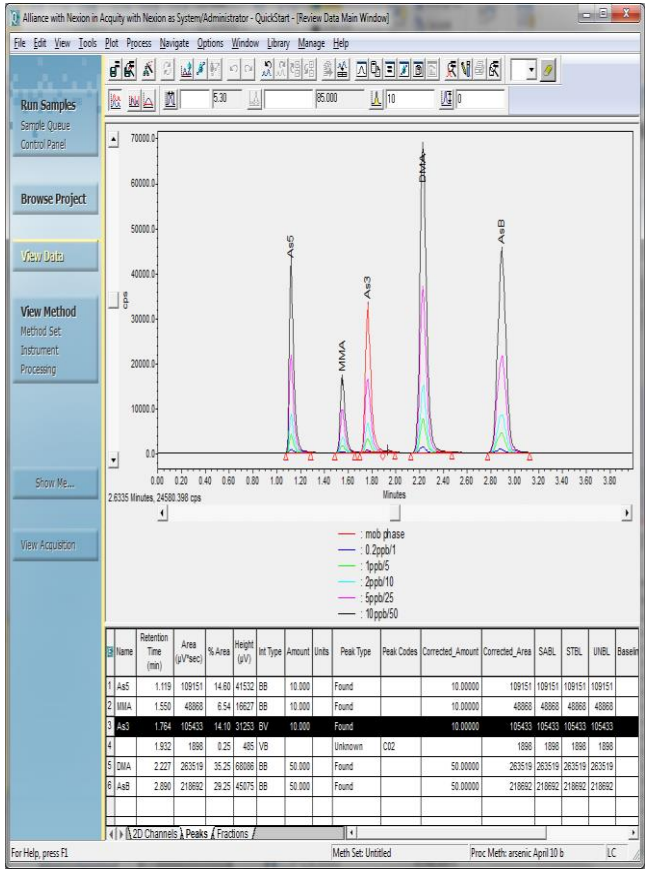
Kalibrier-kurve

Details

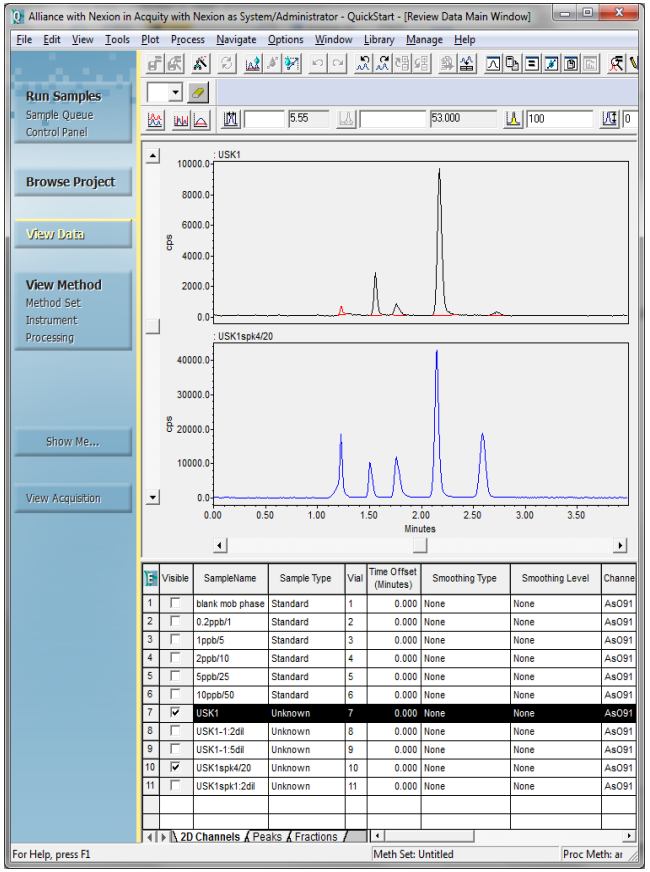
PerkinElmer

Proben vergleichen, auswerten, darstellen

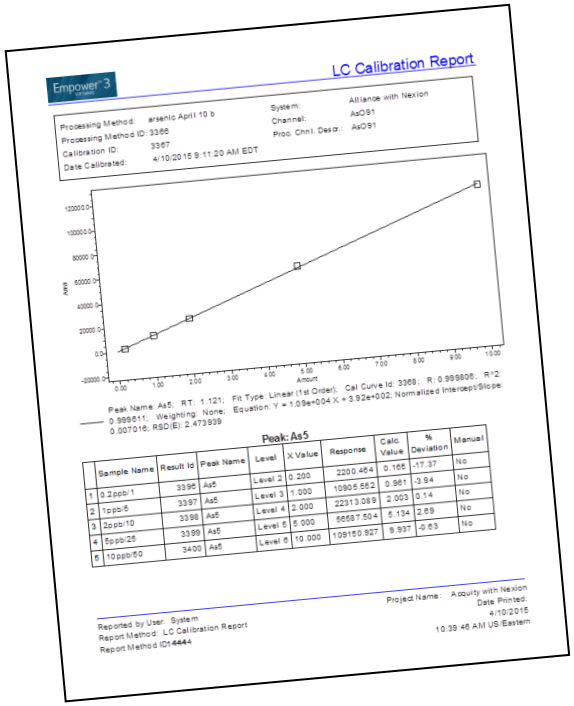
Overlay verschiedener Chromatogramme

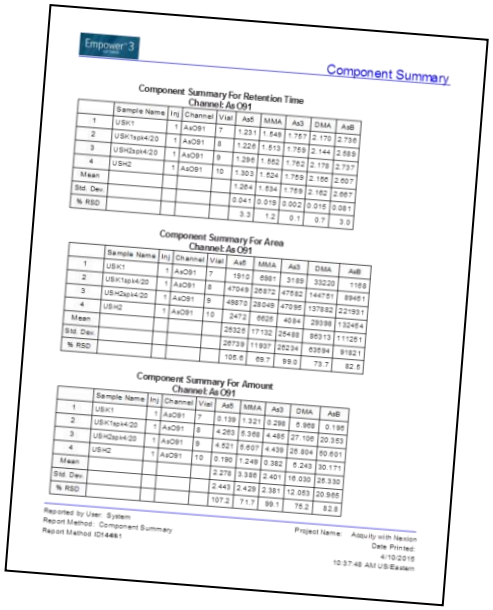


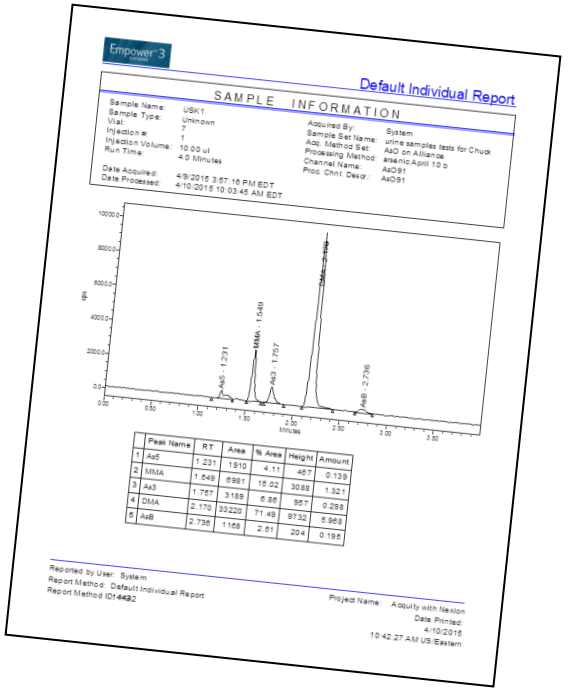
Stapelansicht verschiedener Chromatogramme

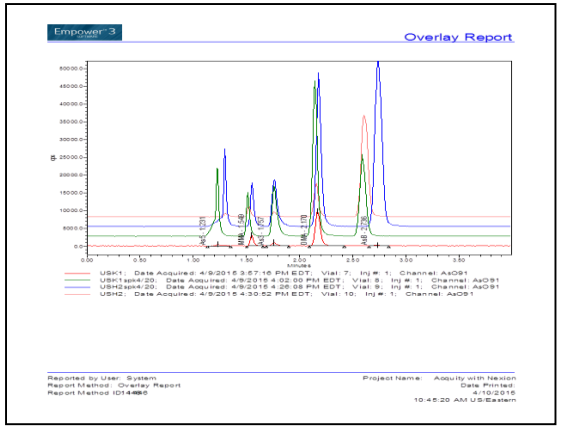


Vielfältige Gestaltungsmöglichkeiten Report/Export


LC Calibration Report


Component Summary


Default Individual Report


Overlay Report

PerkinElmer