

ICP-MS jako detektor ve speciační analýze

Martin Juříček, Manažer servisu

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ICP-MS jako detektor ve speciální analýze

- Speciální analýza
- Spojení separačních technik s ICP-MS
- SW MassHunter 5.1
- Stanovení organocínových sloučenin metodou GC – ICP-MS
- Stanovení selenoproteinů v krysím krevním séru na HPLC – ICP-QQQ



ICP-MS jako detektor ve speciální analýze

Chemická specie – specifická forma prvku definovaná izotopickým složením, elektronovým nebo oxidačním stavem a nebo komplexovou či molekulovou strukturou

Speciální analýza – analytická aktivita spočívající v identifikování a nebo měření množství jedné nebo více individuálních chemických specií ve vzorku

IUPAC Guidelines for Terms Related to Speciation of Trace Elements, Pure Appl. Chem., 72/8 (2000) 1453-1470.



ICP-MS jako detektor ve speciální analýze

Chemická specie – specifická forma prvku definovaná izotopickým složením, elektronovým nebo oxidačním stavem a nebo komplexovou či molekulovou strukturou

Specie se liší:

- chemickým složením
- chemickými vlastnostmi
- chováním v organismu
- účinky na organismus
- **toxicitou**



ICP-MS jako detektor ve speciální analýze

Prvková speciální analýza

úprava vzorku

derivatizace, extrakce, komplexace, odstranění maticních komponent, generování hydridů...

separace specií

online - HPLC, GC, CE...; offline

detekce specií

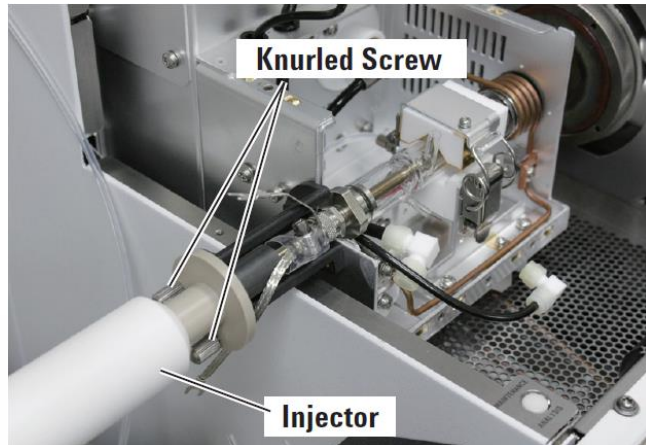
AAS, AFS, chemosensory, ICP-MS

*rychlost, citlivost, selektivita, přesnost, správnost, **robustnost***

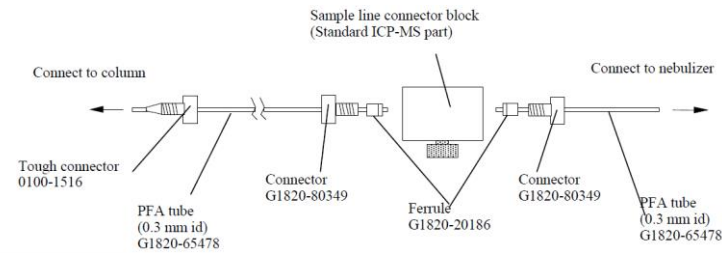


ICP-MS jako detektor ve speciální analýze

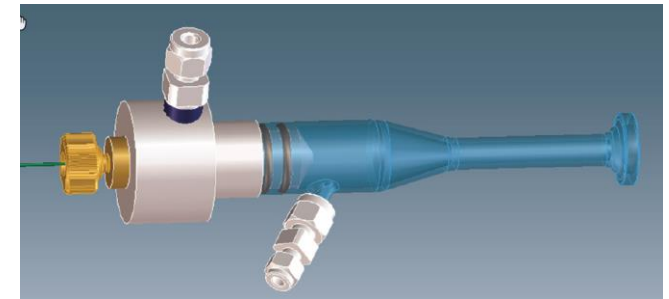
GC-ICP-MS interface
G3158D



HPLC-ICP-MS connection kit
G1833-65200



CE-ICP-MS capillary LC
connection kit G3680A



ICP-MS MassHunter 5.1 s chromatografickou nastavbou

The screenshot displays the ICP-MS MassHunter 5.1 software interface. At the top is a ribbon menu with tabs for File, Home, View, Report, and Tools. The Home tab is active, showing icons for Sample Handling (Nebulizer Pump Speed, Autosampler), Startup (Plasma, Configuration, Skip Warming up), Tune (Set as Global Tune), Batch (New, Open, Create From Template, Save As, Add to Queue, Advanced Option), and Acquisition Queue (Resume, Pause, Stop). The title bar on the right reads "Data acquisition SW".

On the left is a "Task Navigat..." sidebar with a "Vacuum on" indicator. The sidebar is organized into sections: Hardware (Dashboard, Performance Report, Maintenance Log, Diagnostics, Nebulizer Test, Torch Axis Setting, Plasma Correction, Ion Lenses Maintenance, Cell Maintenance, Resolution/Axis, P/A Factor Setting, EM Setting, Dead Time Calibration), Startup (Startup Configuration, User Tune Configurator), and Acquisition (Setup, Tune Modes, Element Selection, Sample Introduction, Monitor).

The main area is titled "Dashboard" and features a series of icons representing the instrument's components, each with a checkmark below it: Mainframe, LC1200, Sample Introduction, Plasma, Ion Lenses, Collision/Reaction Cell, Quadrupole, and Detector.

Below the dashboard is the "Early Maintenance Feedback" section, which includes a "Setting" button and two main areas: "User Maintenance Counters" and "Instrument Counters".

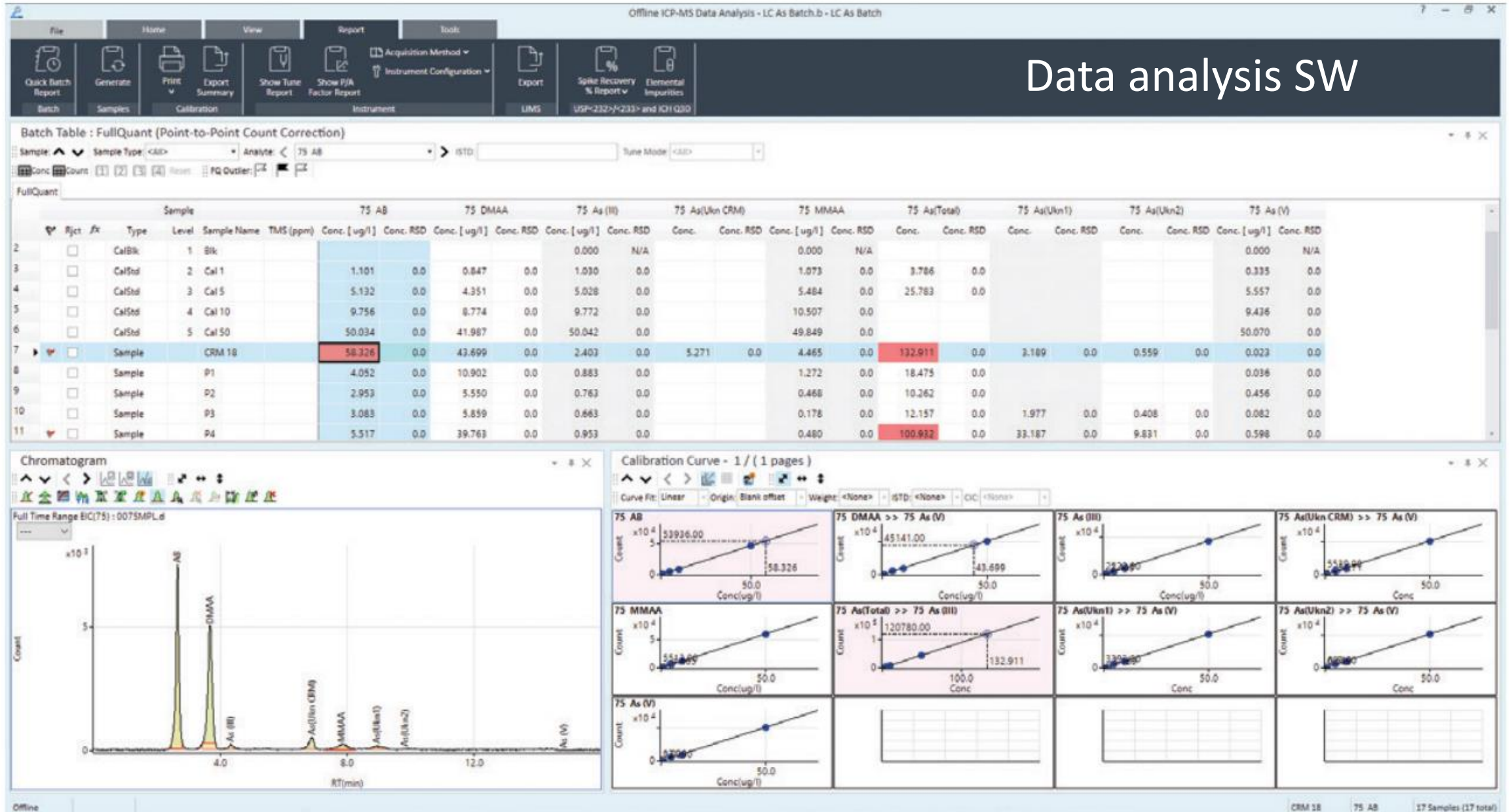
User Maintenance Counters:

- Check Foreline Pump Oil: Vacuum ON Days: 5/30 (Reset)
- Change Foreline Pump Oil: Vacuum ON Days: 6/180 (Reset)
- Change Oil Mist Filter: Vacuum ON Days: 6/360 (Reset)
- Change Sample Uptake Tube: Solutions Measured: 0/200 (Reset)
- Clean Sampling Cone: Solutions Measured: 0/200 (Reset)
- Clean Skimmer Cone: Solutions Measured: 0/200 (Reset)

Instrument Counters:

- Power ON Days: 21
- Plasma ON Days: 20
- Foreline Pump Days: 21
- Turbo Pump Days: 21
- Solutions Measured: 0

ICP-MS MassHunter 5.1 s chromatografickou nastavbou



Data analysis SW

Stanovení organocínových sloučenin metodou GC – ICP-MS

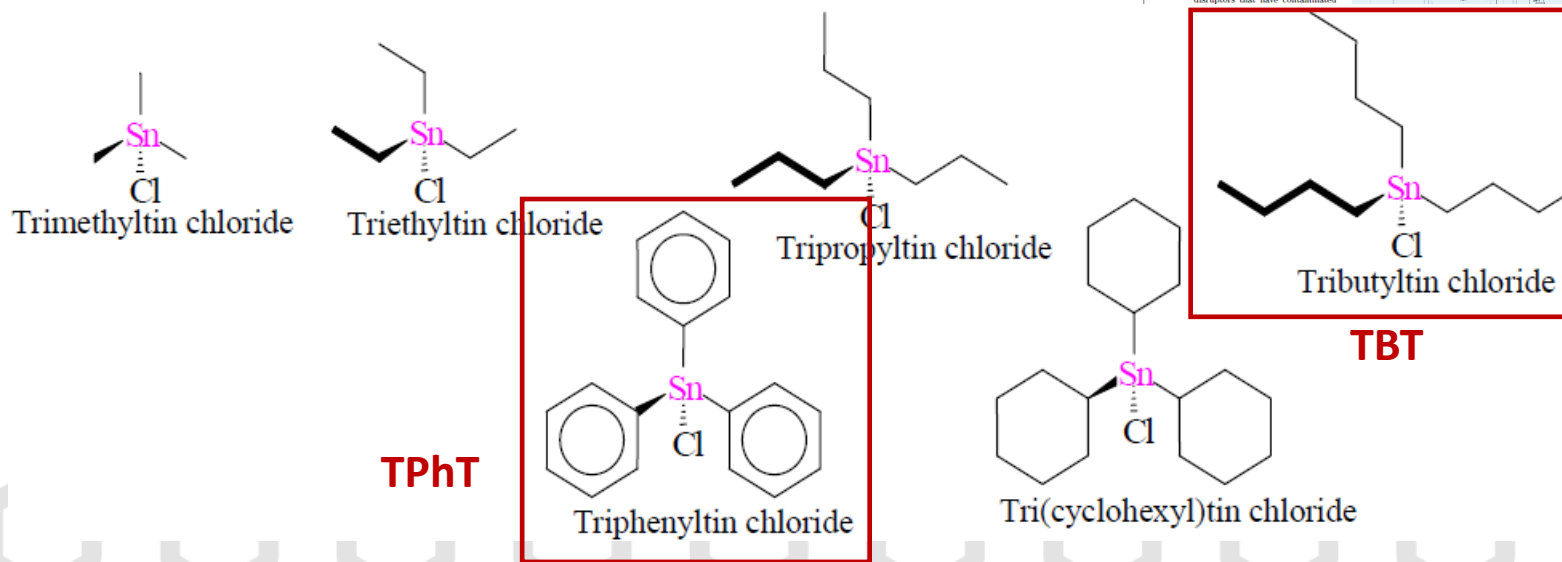
mono- a di-substituované organocínové sloučeniny

změkčovadla a stabilizátory PVC (obaly, potrubí...)

tri-substituované organocínové sloučeniny

biocidní přípravky, ochrana konstrukcí před řasami a mlži = antifouling

biologicky aktivní, hormonálně aktivní látky



Ultrasensitive High Throughput Elemental Speciation Analysis using GC-ICP-MS

Eckard Jentzen, Jasmin Miago, Jürgen Kuballa, Sabrina Sievers
Hilt Department, GALAB Laboratories, Hamburg, Germany

Figure 1. Calibration curve for tributyltin from 2 to 100 ng/L (ppb).

GALAB is an independent service laboratory that analyzes and evaluates contaminant elements and compounds in food, food packaging, sanitary products, industrial products, biopharmaceutical products, and environmental samples. We are well-equipped with the latest analytical equipment, and use a broad range of standard and tailored analytical methods to provide our clients with high-quality data. Our analytical database comprises more than 2000 single substances and more than 1000 different analytical methods. Despite this range, we are constantly developing new methods on behalf of our clients to ensure the quality and safety of their products.

Speciation of organotin compounds
Organometallic species may occur naturally in the environment or be present as a result of human activity [1]. Organometallic compounds are often more bioavailable and toxic than inorganic compounds of the same element. This is especially true for organotin compounds (OTCs), such as tributyltin (TBT) and triphenyltin (TPHT). Tributyltin OTCs are extensively used as biocides in agrochemicals, antifouling paints, wood preservatives and for material protection. Mono-alkyl and dialkyl tin compounds are widely used as PVC stabilizers in packaging and coating materials, foils and various types of piping [2]. Both TBT and TPHT are well-known endocrine disruptors that have contaminated

contaminants. Actual or expected changes to the regulatory framework create a demand for more sensitive and robust analytical procedures. In this article, a sensitive, high-throughput technique is presented for the detection of organometallic species in different matrices.

Currently, most laboratories use GC with MSD, PPD, or AED for the detection of organometallic compounds. Some of these techniques offer the required sensitivity, stability, or robustness to most evolving environmental requirements. However, ultrasensitive high-throughput elemental speciation analysis (UHTESA) is now possible using GC-ICP-MS with a suitable sample preparation technique [5].

Experimental
Reagents and samples
Analytical grade reagents were bought from Merck, Germany, and were used without further purification. Single compound and mixed organotin standards were obtained from Campro Scientific, Germany. Sodium tetraethylborate was from Synthese Nord, Germany.

Instrumentation
An Agilent 7800 GC was coupled to

an Agilent 7900 ICP-MS using the interface (G1315SD). The GC was fitted with an Agilent JAW DB-5ms Ultra Inert column. The ICP-MS was fitted with platinum-tipped interface cones.

Table 1. GC-ICP-MS operating parameters

Parameter	Value
RF power (W)	1100
Injection port temperature (°C)	280
Helium carrier gas flow rate (mL/min)	16.6
Injection volume (µL)	1

Table 2. GC temperature program

Start temp (°C)	50
Heating rate (°C/min)	40
Max temp (°C)	250
Hold time (min)	2

Appropriate sample preparation (extraction and derivatization) techniques are an important prerequisite to the accurate determination of organometallic species by GC. The species must be transformed into their perallylated nonpolar derivatives. A detailed description of the sample preparation steps is given in reference [1].



Stanovení organocínových sloučenin metodou GC – ICP-MS

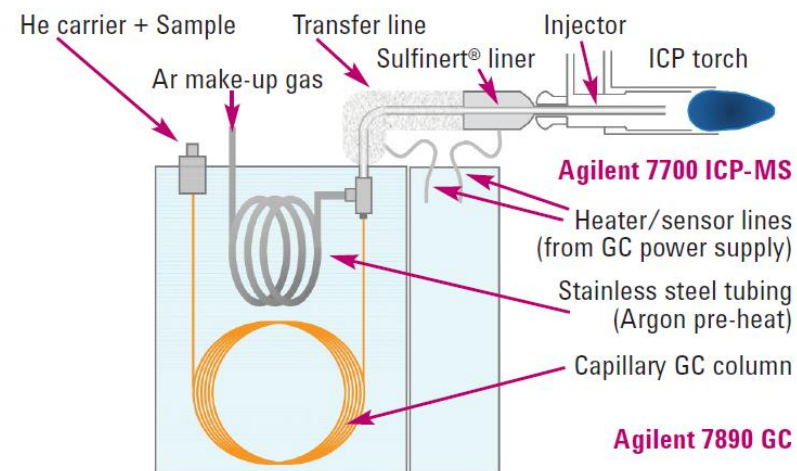
pitná voda, povrchová voda, sediment, rybí maso (treska), PVC hračka

příprava vzorků

alkylace NaBEt₄



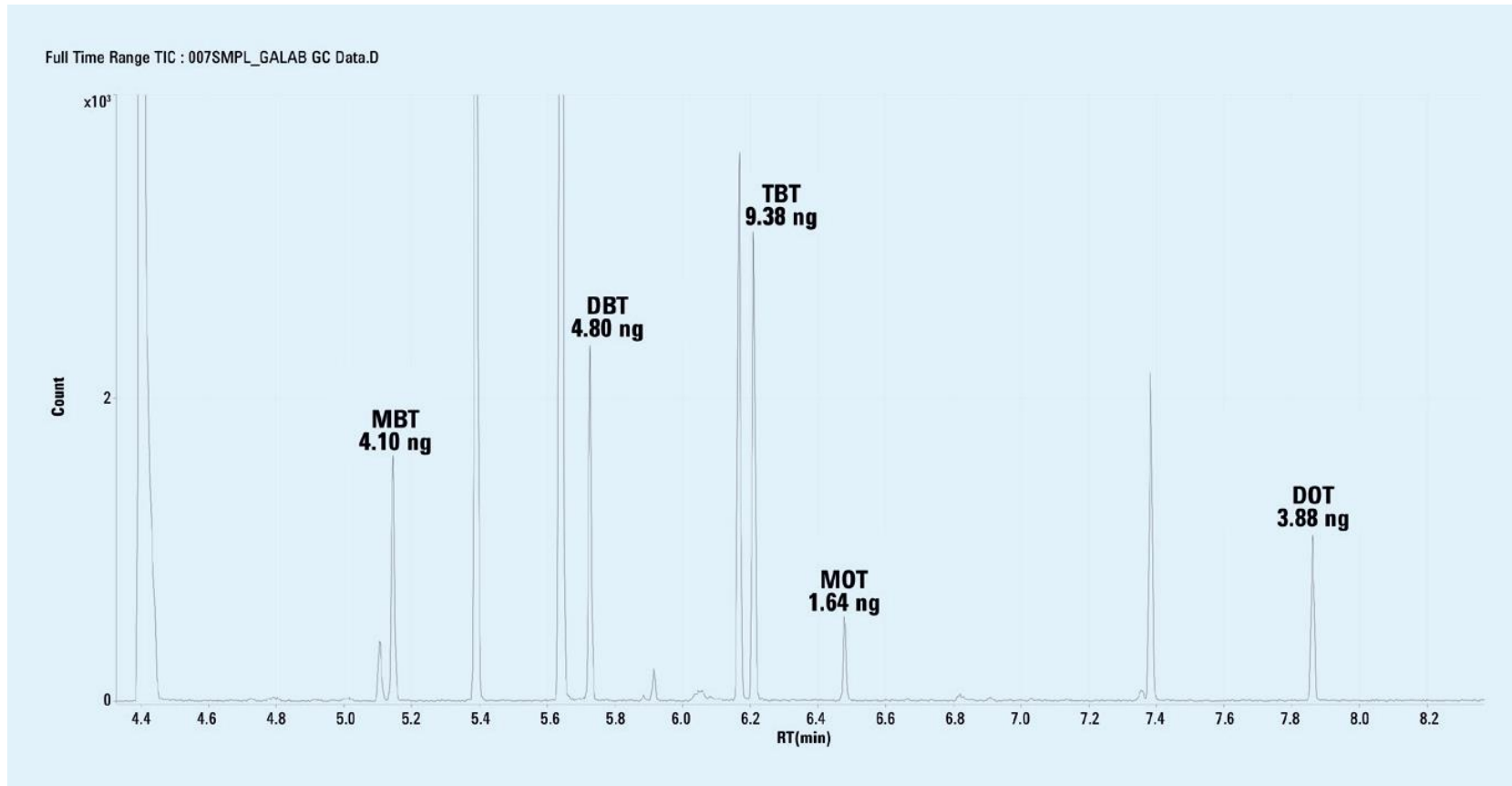
extrakce do hexanu



GC 7890	
column	DB-5ms <i>Ultralnert</i>
carrier gas	He
carrier flow rate (ml / min)	19.6
injection volume (μl)	1
inlet temp (°C)	280
start temp (°C)	50
heating rate (°C /min)	40
max temp (°C)	320
hold time (min)	3

ICP-MS 7900	
cones (sampling + skimmer)	Pt
carrier gas (l/min)	0.95
plasma gas (l/min)	15.00
sampling depth (mm)	7.0
RF (W)	1100
ORS ⁴ He gas flow (ml/min)	4.0
mass	118
integration time per point (s)	0.1

Stanovení organocínových sloučenin metodou GC – ICP-MS



ukázkový chromatogram stanovení OTC ve vzorku sedimentu



HPST

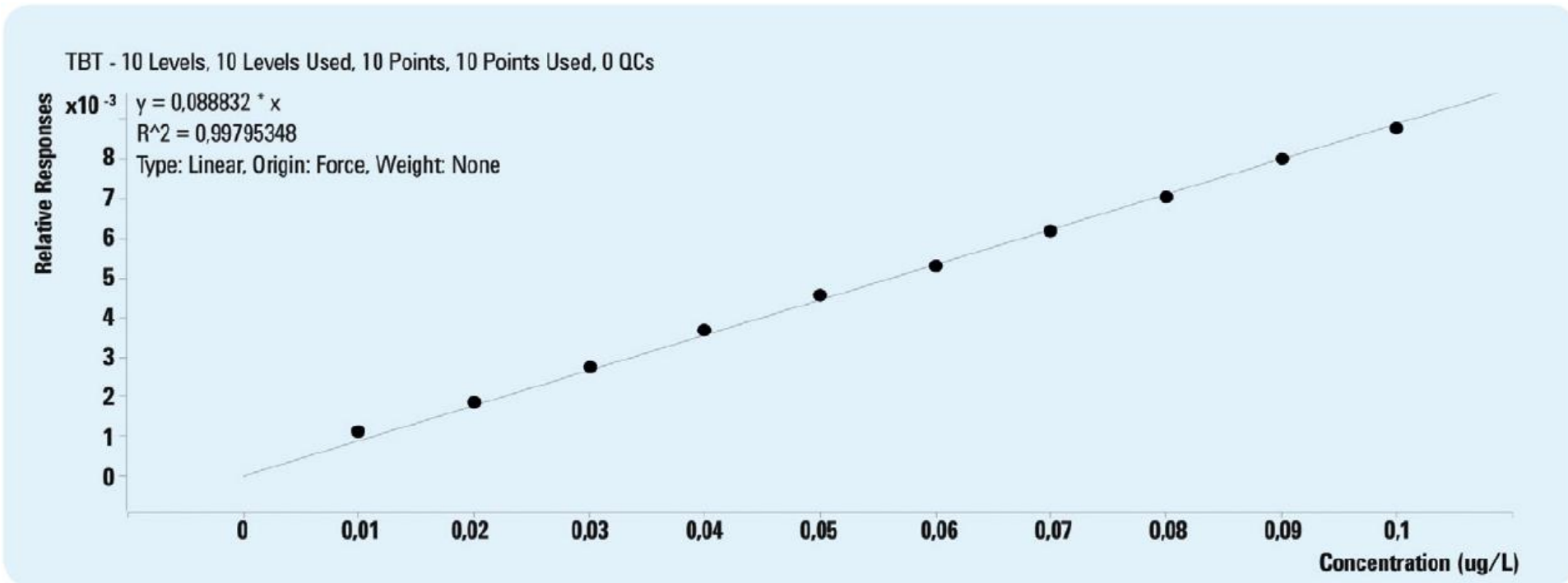


Stanovení organocínových sloučenin metodou GC – ICP-MS

TBT

LOD (3σ SD 10 blanků) = 2 pg/l

LOQ (10σ SD 10 blanků) = 7 pg/l



kalibrační křivka TBT, 0 – 100 ng/l



HPST



Stanovení organocínových sloučenin metodou GC – ICP-MS

2013/39/EU

TBT surface water annual average < 0.2 ng/l

OTC	RT, min	Sample and concentration				
		Drinking water, ng/L	Surface water, ng/L	Sediment, µg/kg	Fish, µg/kg	PVC toy, µg/kg
Monobutyltin (MBT)	5.13	0.07	1.66	4.1	0.35	14.01
Dibutyltin (DBT)	5.71	0.06	0.75	4.8	0.71	55.04
Monophenyltin (MPT)	6.03	<0.01	0.16	<0.1	<0.01	<1
Tributyltin (TBT)	6.22	<0.01	1.05	9.38	0.05	3.16
Monooctyltin (MOT)	6.49	0.01	0.15	1.64	0.04	<1
Tetrabutyltin (TTBT)	6.53	<0.01	<0.01	<0.1	<0.01	<1
Diocetyltn (DOT)	7.74	<0.01	0.015	3.88	0.01	<1
Triphenyltin (TPhT)	8.31	<0.01	0.07	<0.1	0.07	<1
Tricyclohexyltin (TcHT)	8.35	<0.01	<0.01	<0.1	<0.01	<1

výsledky stanovení OTC v různých maticích (po přepočtu zředovacího faktoru z extrakce)



Stanovení organocínových sloučenin metodou GC – ICP-MS

GC 7890 + ICP-MS 7900

- přesná, robustní, opakovatelná, vysoce citlivá metoda stanovení OTC
- rychlá – 10 OTCs < 10 minut
- splňuje 2013/39/EU (0.2 ng/l) pro monitoring obsahu OTC v povrchových vodách
- vhodná pro širokou škálu matric



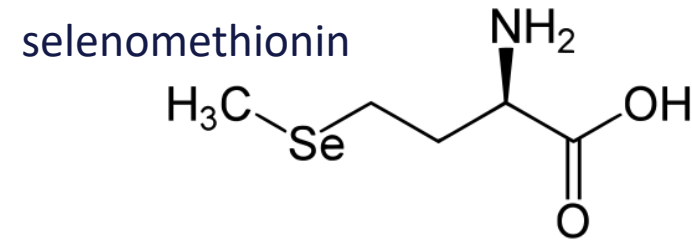
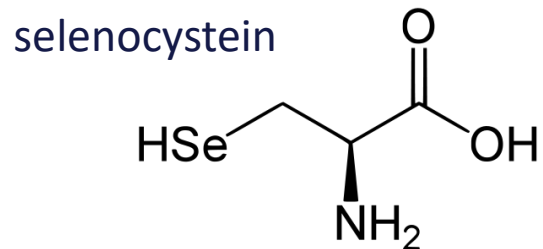
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Stanovení selenoproteinů v krysím krevním séru na HPLC – ICP-QQQ

Selen důležitý biogenní prvek

v tělním prostředí v esenciálních aminokyselinách



Extracellular glutathion peroxidasa (eGPx)

Selenoprotein P (SeIP)

Albumin protein krevní plazmy (60% bílkovin)

transport MK, minerálů

udržuje v těle stálé vnitřní prostředí



Stanovení selenoproteinů v krysím krevním séru na HPLC – ICP-QQQ

Se – zatížen značnými spektrálními interferencemi

mass	abundance (%)	interference
76	9.37	38Ar38Ar
77	7.63	40Ar37Cl, 40Ca37Cl
78	23.77	40Ar38Ar, 40Ca38Ar
80	49.61	40Ar40Ar, 40Ca40Ar, 79Br1H
82	8.73	81Br1H

+ M^{II+} vzácných zemin

amu 152 – 164 (Sm, Gd, Dy)



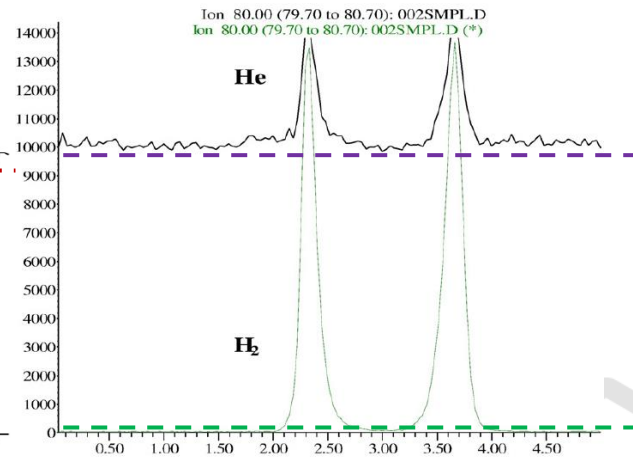
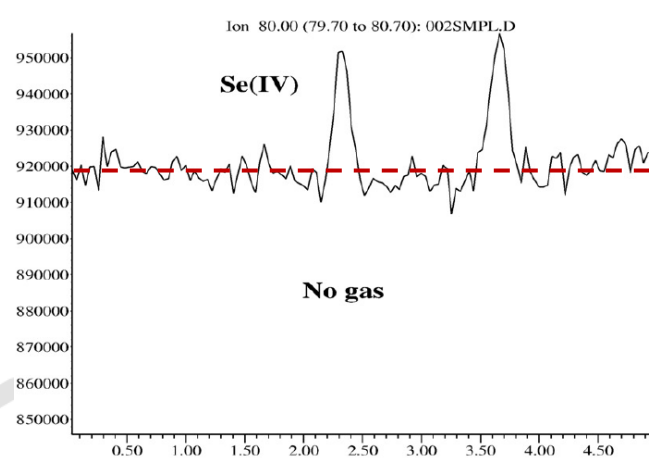
Nogas nepoužitelný

He málo citlivý

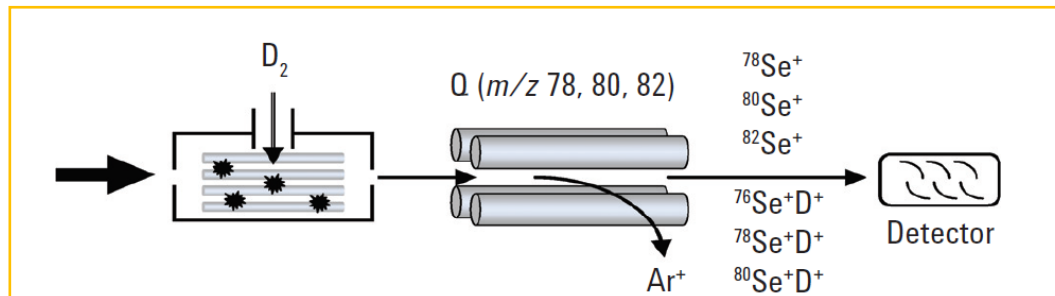
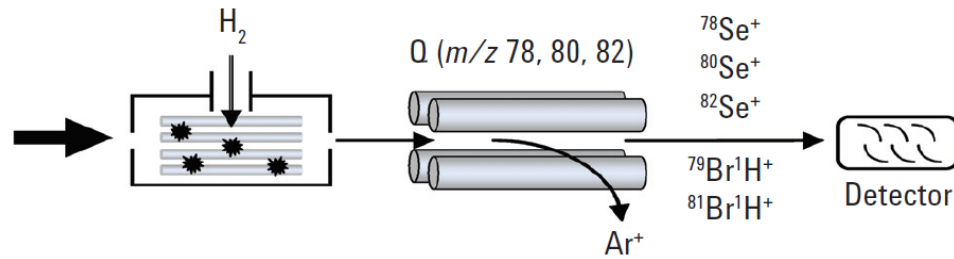
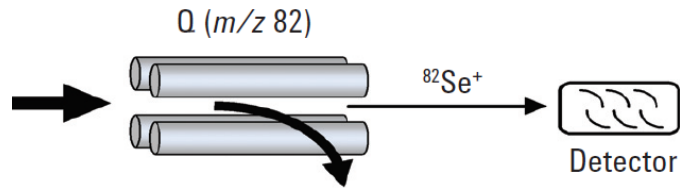
H₂ výborné potlačení interferencí

zachování dobré citlivosti

tvorba nových interferencí



Stanovení selenoproteinů v krysím krevním séru na HPLC – ICP-QQQ

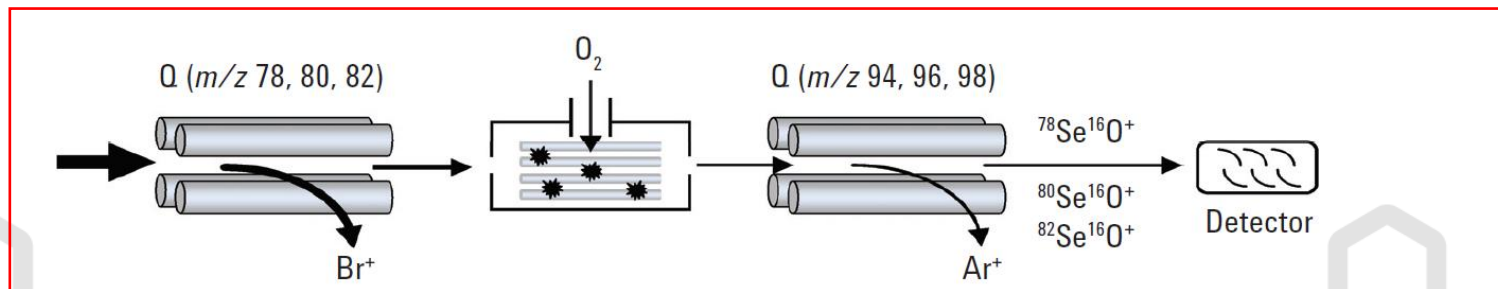


ICP-MS 7700

reakční plyn D_2

+2 amu

*potlačení
interferencí
Br*



ICP-QQQ

O_2 + 16 amu

Stanovení selenoproteinů v krysím krevním séru na HPLC – ICP-QQQ

Příprava vzorků:


krysy Wistar, samečci 5 týdnů, Specific Patogen Free

odběr krve, centrifugace 1600 x g 10 minut

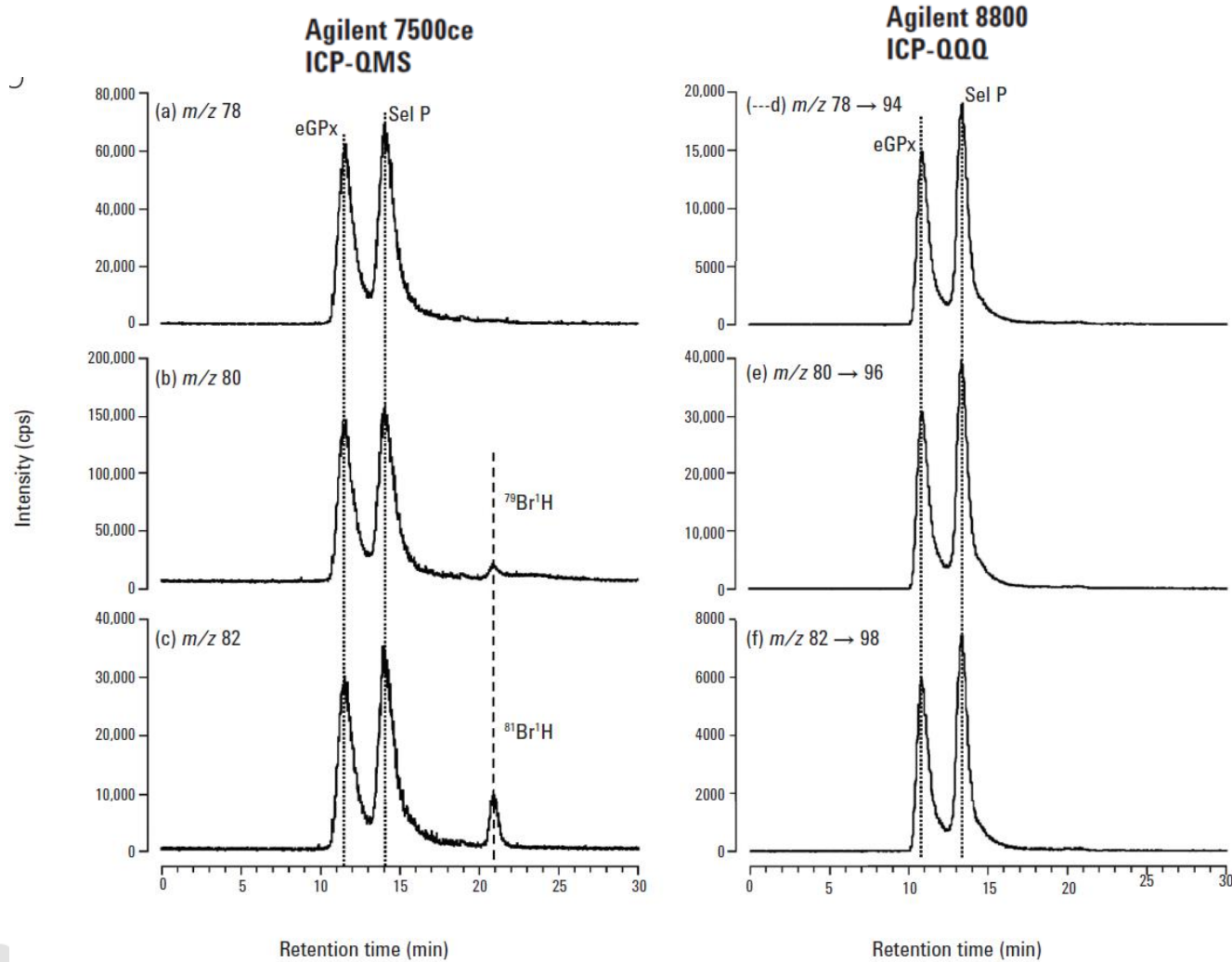
HPLC separation	
sample loop (μ l)	200
guard column	7.5mm ID x 75mm Showa Denko
column	MM gel column 7.5mm ID x 300mm, GS-520HQ
MF	50mmol/l Tris-HCl, pH 7.4, 0.6 ml/min



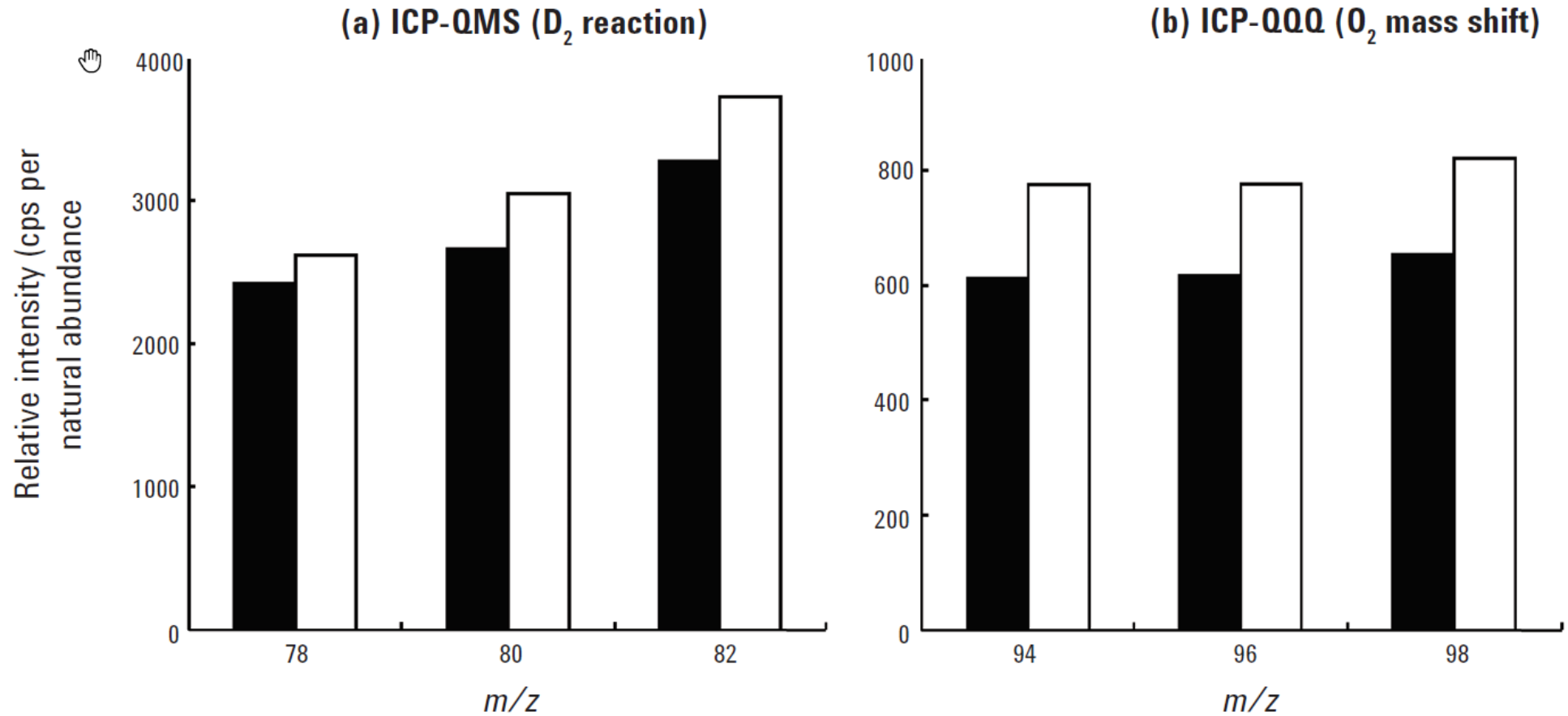
Stanovení selenoproteinů v krysím krevním séru na HPLC – ICP-QQQ

	Agilent 7500ce ICP-QMS	Agilent 8800 ICP-QQQ
Plasma setting		
RF power (W)	1450	1550
Nebulizer type	Babington	MicroMist
Nebulizer gas flow (L/min)	1.15	0.90
Make-up gas flow (L/min)	0.11	0.25
Plasma gas flow (L/min)	15.0	14.0
Reaction/Collision cell		
D ₂ gas flow (mL/min)	3.0	-
O ₂ gas flow (mL/min)	-	0.3
Data acquisition		
<i>m/z</i> monitored 	76 to 84	
		94 shifted from 78
		96 shifted from 80
		98 shifted from 82

Stanovení selenoproteinů v krysím krevním séru na HPLC – ICP-QQQ



Stanovení selenoproteinů v krysím krevním séru na HPLC – ICP-QQQ



Stanovení selenoproteinů v krysím krevním séru na HPLC – ICP-QQQ

dobrá separace dvou hlavních selenoproteinů přímo z krevního séra na HPLC

porovnání ICP-QMS a ICP-QQQ ?

ICP-QQQ



přesnější a správnější výsledky



účinné odstranění matricových i spektrálních interferencí



výrazně lepší odstup Signál / Šum



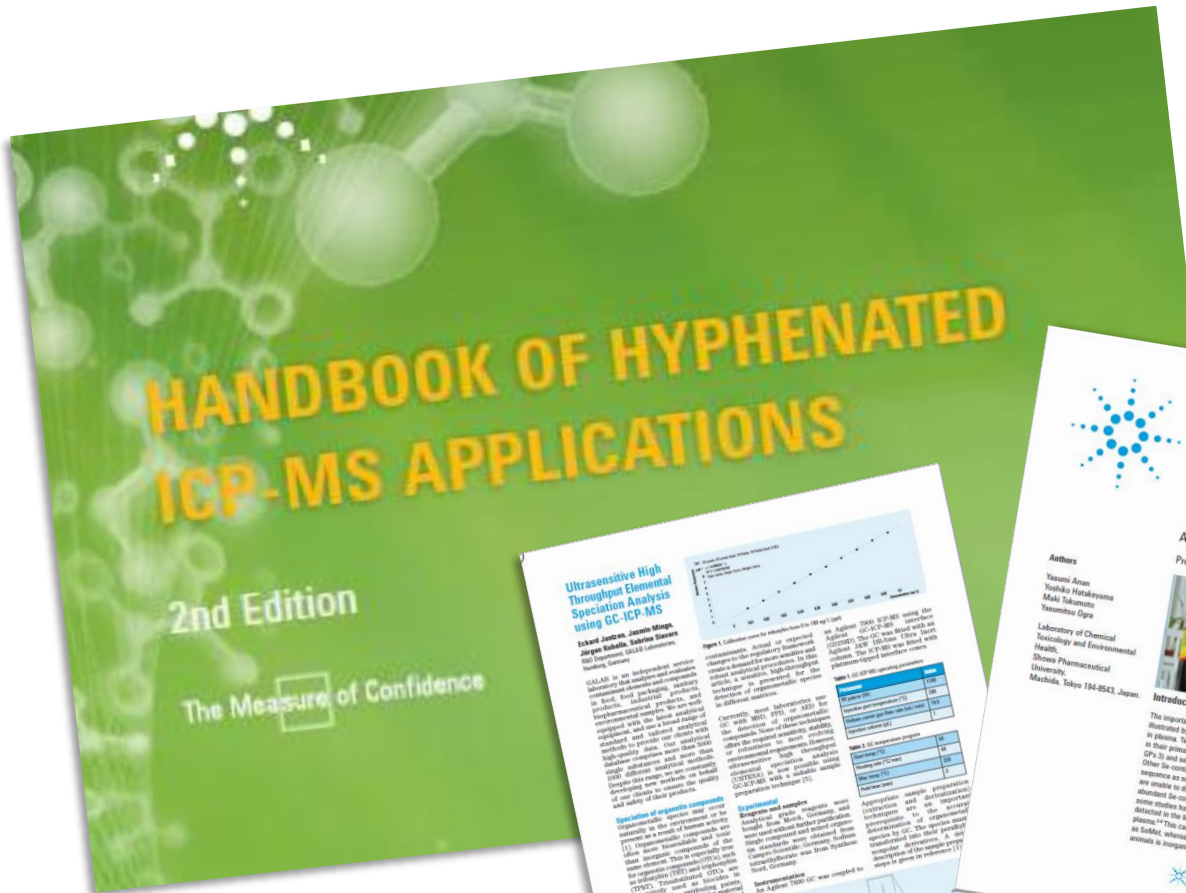
výrazně lepší LOD a LOQ



HPST



ICP-MS jako detektor ve speciální analýze



Ultrasensitive High Throughput Elemental Speciation Analysis using GC-ICP-MS
Richard J. Austin, James M. Edwards, Jürgen Knebel, Sabine Evers, Hans-Joachim Löffler, Gerd-Ludwig Fisher, Wolfgang Scharn

Application note
Analysis of selenoproteins in rat serum by Triple Quadrupole ICP-MS

Authors: Yasumi Arai, Yoshiko Hatakeyama, Maki Tokumoto, Yasuhiro Ogra, Laboratory of Chemical Technology and Environmental Health, Showa Pharmaceutical University, Machida, Tokyo 194-8543, Japan

Abstract: The importance of selenium (Se) as an essential micronutrient to animals is illustrated by the fact that it is present in several of the key proteins found in their primary structures, selenocysteine (Se-Cys) and selenoprotein P (Se-P). Other Se-containing proteins which have been identified in animal plasma, are selenomethionine (Se-Met), selenocystathionine (Se-Cys₂), and selenomethionine (Se-Met). The most abundant Se-containing protein in human plasma is selenomethionine (Se-Met). However, some studies have indicated that no little Se containing albumin is present in the blood plasma of experimental animals compared to human plasma. This can be explained by the fact that humans ingest Se mainly as Se-Met, whereas the major Se species in the study given to experimental animals is inorganic Se, such as selenite and selenate.

Figure 1: Calibration curve for selenite (Se-IV) at 100 ng/L level. The graph shows a linear relationship between concentration and signal intensity.

Table 1: LOD and LOQ of selenoproteins

Selenoprotein	LOD (ng/L)	LOQ (ng/L)
Se-P	0.05	0.1
Se-Cys ₂	0.05	0.1
Se-Met	0.05	0.1

Figure 2: In separation of a standard mixture of selenoproteins at 1.0 ng/L level. The chromatogram shows distinct peaks for each selenoprotein.

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Děkuji za pozornost !

