GENEROVÁNÍ TĚKAVÝCH SLOUČENIN
PRO STOPOVOU PRVKOVOU A SPECIAČNÍ ANALÝZU:
VÝHODY A OMEZENÍ

Ústav analytické chemie AVČR, v. v. i.

Oddělení stopové prvkové analýzy

Akademie věd České republiky

iac brno

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GENERATION OF VOLATILE SPECIES

- volatile compounds generation (VCG) / volatile species (VSG)
- **selective conversion of analyte to volatile compound**
- VSG compatible with all spectrometric techniques
- VSG independent of the detector used
- most commonly used for hydride forming elements (HG)

VSG → AAS, AFS, ICP-OES, ICP-MS

As
Sb
Bi
Se
Te
Pb
Sn
Ge

GENERATION OF VOLATILE SPECIES

- **selective conversion of analyte to volatile species**
  - analyte separation from the matrix (interferences minimized)
  - high transport efficiency of analyte into the detector → lower LOD

- analyte preconcentration in gaseous phase → further LOD improvement

- speciation analysis without chromatography feasible

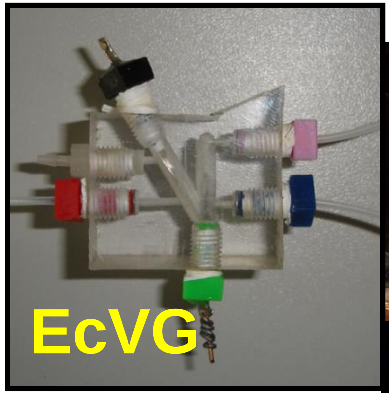
APPROACHES TO VSG

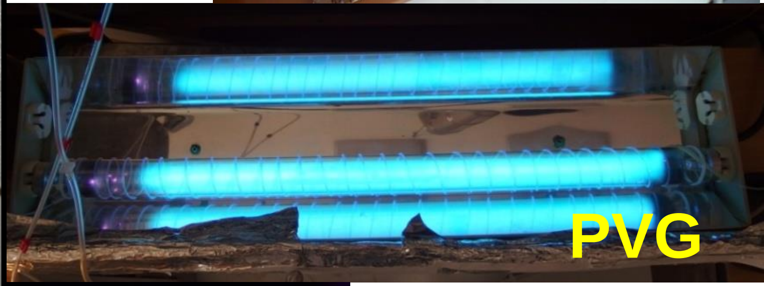
- **Chemical generation (CVG)**
  - analyte reduction by chemical reaction ($HCl/NaBH_4$)
  - high generation efficiency (~ 100 %)

- **Electrochemical generation (EcVG)**
  - analyte reduction by current
  - low generation efficiency
  - potential to reach low LOD

- **Photochemical generation (PVG)**
  - analyte reduction by UV radiation

- **Plasma mediated vapor generation (PMVG)**
  - **interaction with plasma - radicals, excited/metastable species, ions**





OUTLINE

- **VSG of non-hydride forming element – Cd**
- **Novel hydride atomizers for AAS based on DBD plasma**
- **VSG-based speciation analysis (Hg, Te, Ge, As)**
- **VSG of mercury based on PMVG of Hg**

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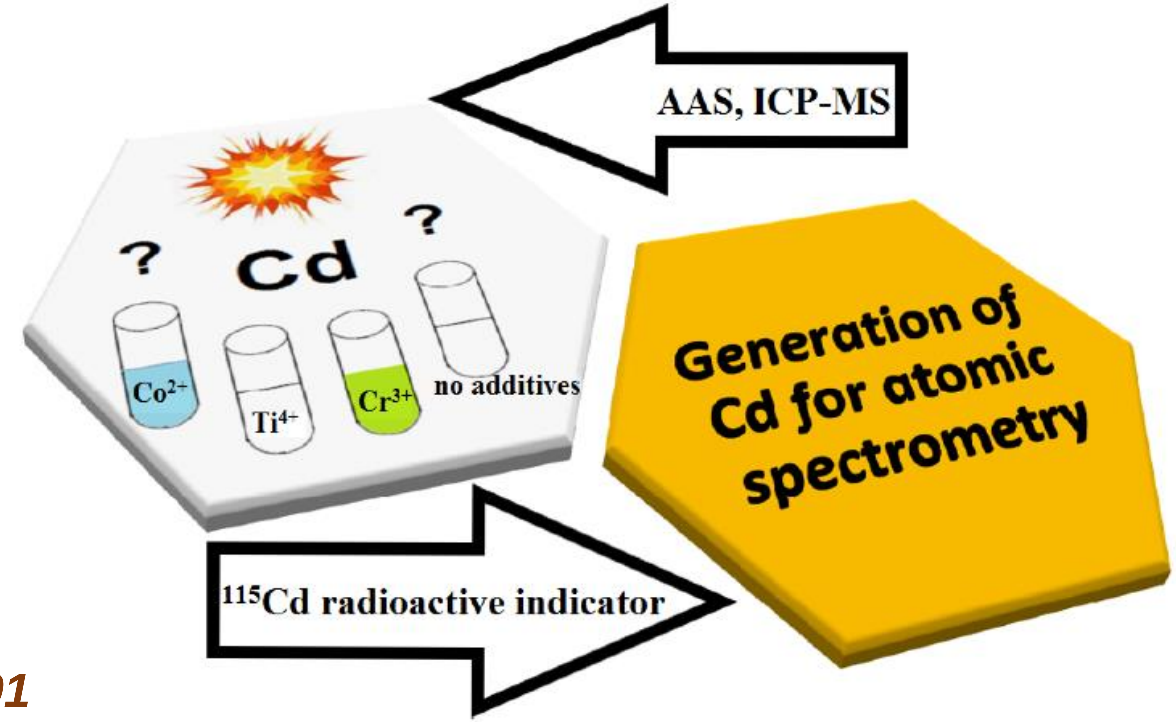
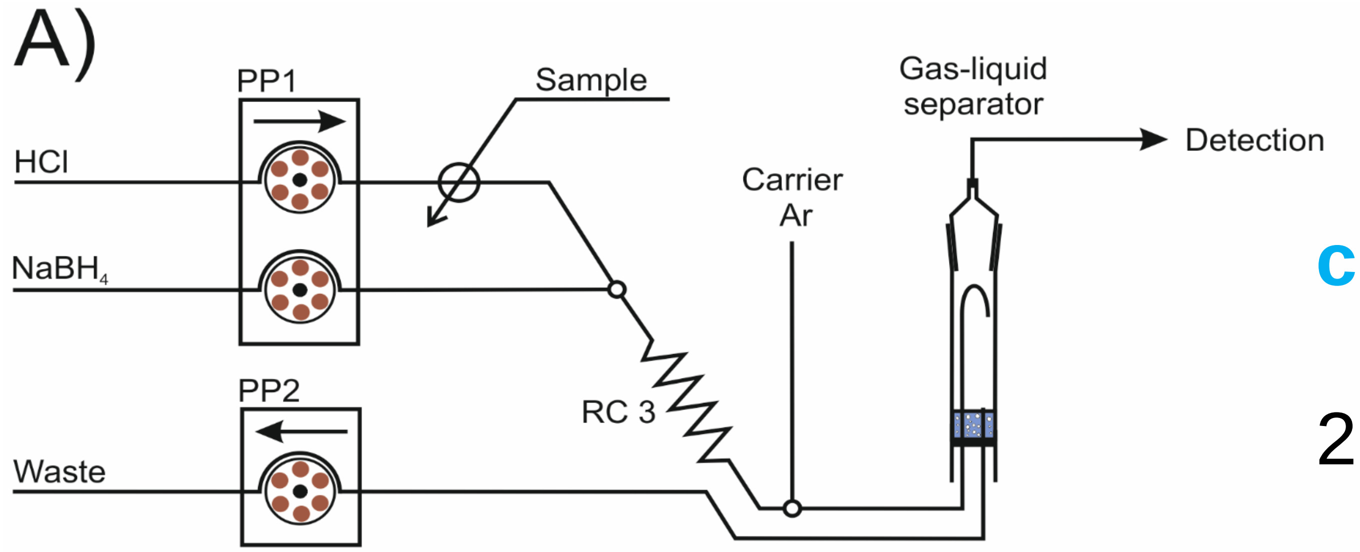
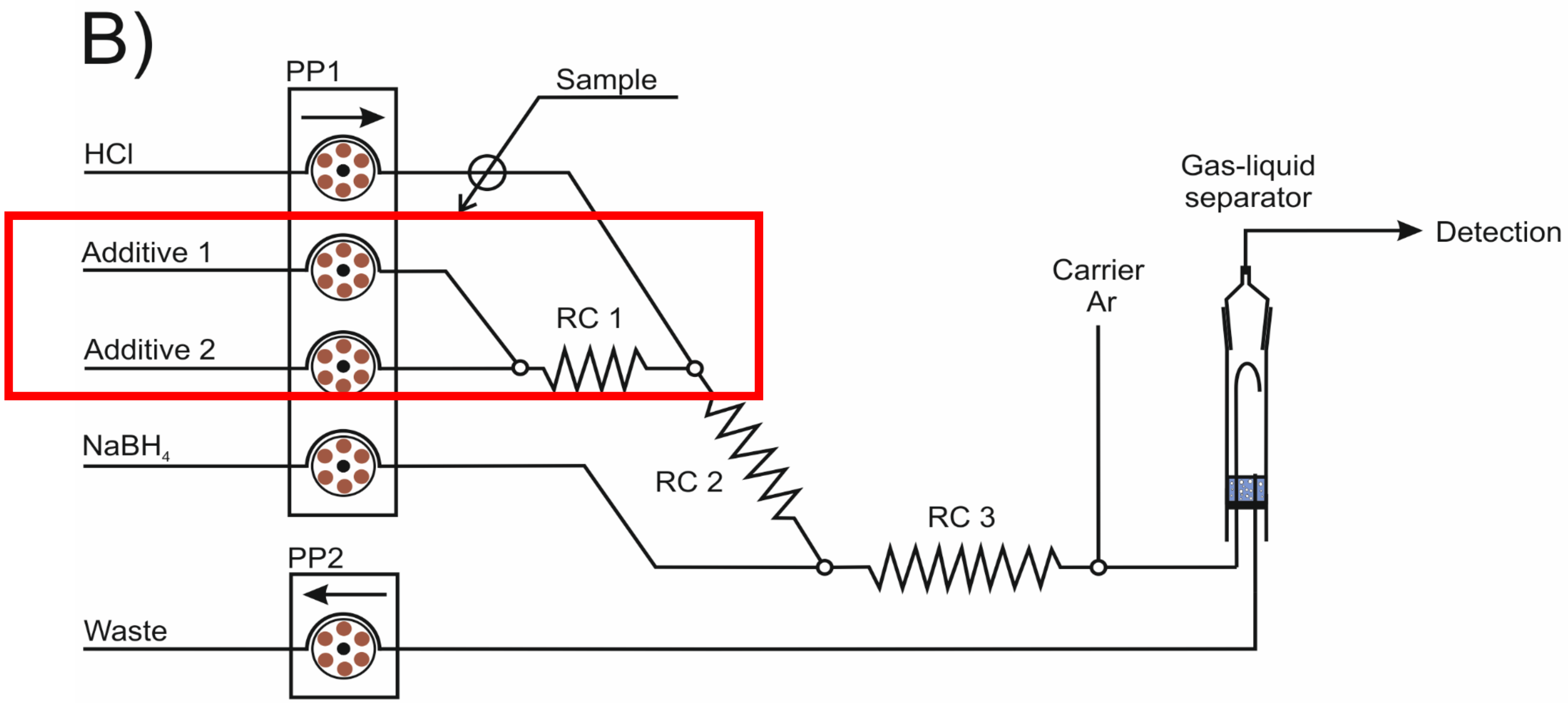


L. Sagapova et al., Anal. Chim. Acta 1168 (2021) 338601



conventional approach: HG

2-channel system ($HCl/NaBH_4$)



VSG of Cd

4-channel system

0.1 mol L^{-1} KCN

0.001 mol L^{-1} Cr^{3+}

- generation efficiency quantified (with additives)
  - by ^{115m}Cd radioactive indicator 66 ± 4 %
  - by comparison of PN-ICP-MS and VSG-ICP-MS 55 ± 2 %

- $HCl/NaBH_4$ without additives < 5%

- Cd free atoms (dominant species) + molecular/aerosol-associated

- VSG-AAS LOD 60 pg mL^{-1} Cd

- VSG-AFS LOD 0.42 pg mL^{-1} Cd

VSG-AFS of Cd – METHOD VALIDATION

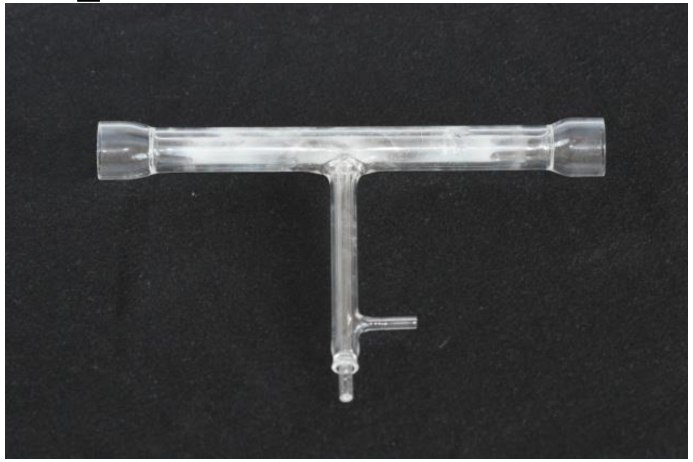
CRM	certified value (ng mL^{-1})	found value (ng mL^{-1})
NIST 1643 f	5.85 ± 0.13	5.90 ± 0.44
ERM-CA 713	5.00 ± 0.05	5.09 ± 0.20

- VSG of non-hydride forming element – Cd
- **Novel hydride atomizers for AAS based on DBD plasma**
- VSG-based speciation analysis
- VSG of mercury based on PMVG of Hg

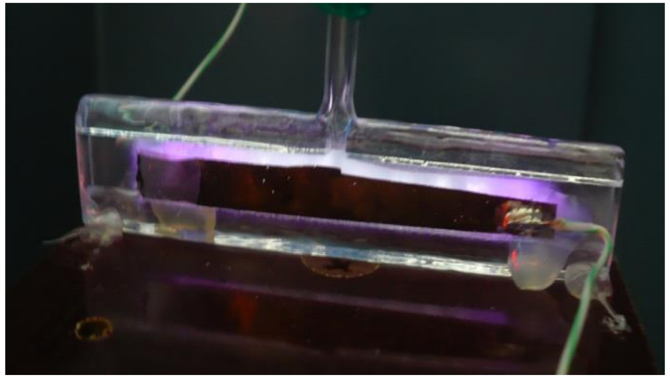
B. Baranová et al., Spectrochim. Acta B, accepted.

HYDRIDE ATOMIZATION - AAS

- **externally heated quartz tube atomizers (QTA)**
  - heated to 900 °C
  - advanced construction (MMQTA) supplied by air/O_2
  - most common hydride atomizer



- **dielectric barrier discharge (DBD) plasmas**
  - low temperature, ambient pressure plasmas
  - AC high voltage
  - novel atomizer



ANALYTICAL FIGURES OF MERIT - SENSITIVITY

Atomizer	Sensitivity, s ng^{-1}					
	Pb	**Bi**	**Sn**	**Se**	**Te**	**As**
(MM)QTA	0.29 ± 0.01	0.40 ± 0.02	0.33 ± 0.01	0.53 ± 0.03	0.32 ± 0.01	0.48 ± 0.01
DBD	0.09 ± 0.01	0.15 ± 0.01	0.05 ± 0.01	0.60 ± 0.04	0.32 ± 0.01	0.54 ± 0.04

- **As, Se, Te – sensitivity reached in DBD comparable to (MM)QTA**
- **Pb, Bi, Sn – (MM)QTA performs much better (3-7 times higher sensitivity)**

- **(MM)QTA** – sensitivity difference among elements: **factor of 2**
- **DBD** - sensitivity difference among elements: **factor of 12**

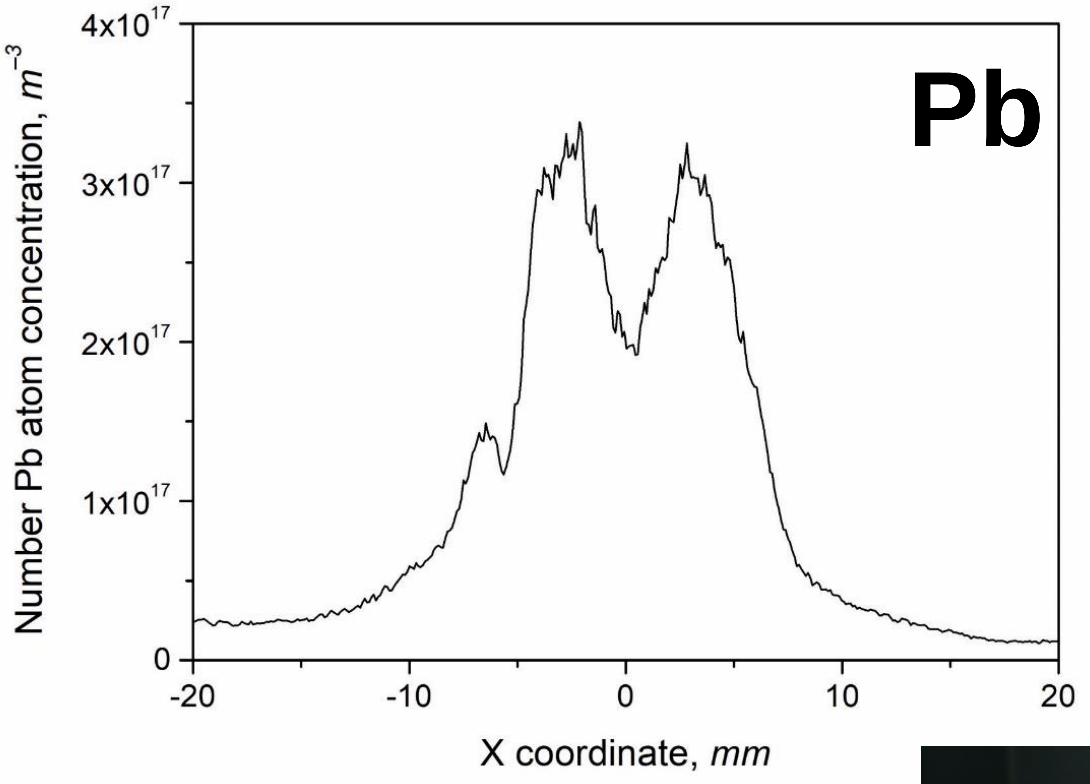
B. Baranová et al., Spectrochim. Acta B, accepted.

L. Juhászová et al., Spectrochim. Acta B 158 (2019), 105630.

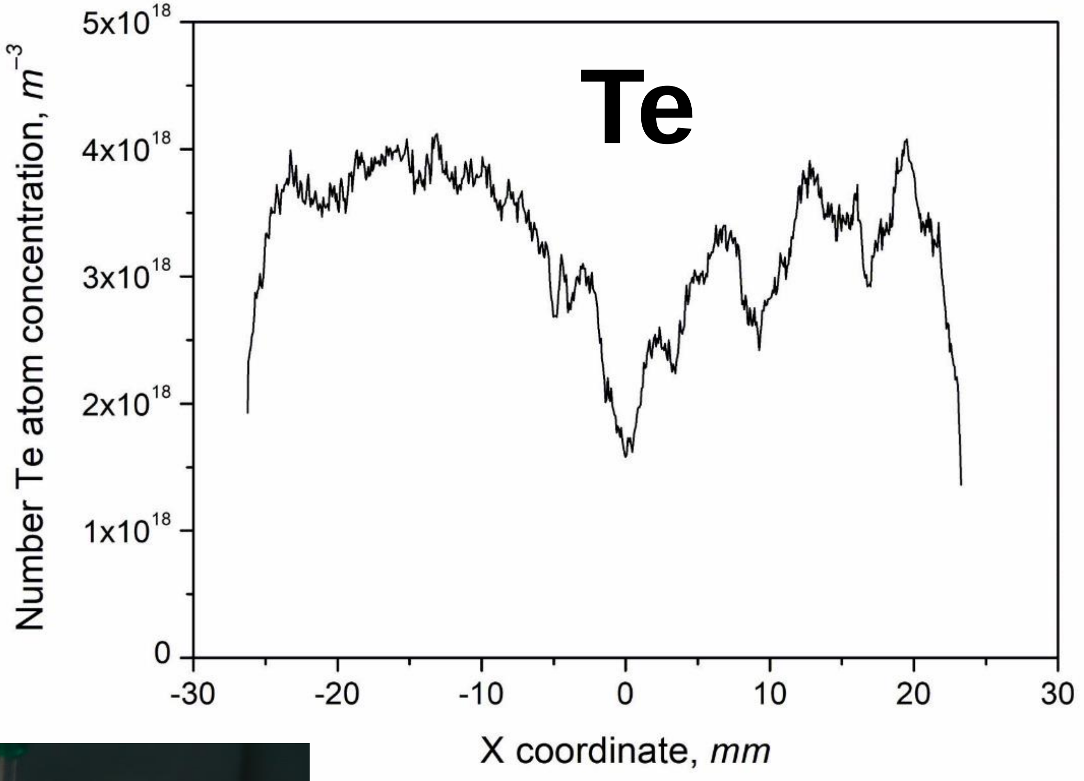
P. Novák et al., Anal. Chem. 88 (2016), 6064-6070.

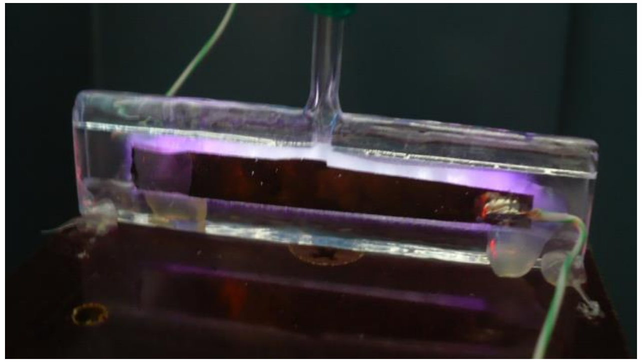
MECHANISTIC STUDIES - LIF

a) **Pb: atomization efficiency 23 ± 7%**



b) **Te: atomization efficiency 100 ± 7%**





M. Albrecht et al., Spectrochim. Acta B 166 (2020) 105819.

K. Bufková et al., Spectrochim. Acta B 171 (2020) 105947.

Mechanistic studies – DEPOSITED FRACTION

leaching experiments, ICP-MS detection

Analyte	Analyte fraction (%) deposited in the atomizer DBD	(MM)QTA
Pb	91 ± 5	107 ± 4
Bi	94 ± 1	92 ± 3
Se	26 - 43	15 ± 2
Te	62 ± 2	37 ± 2

- fast decay of Pb and Bi free atoms → deposit formation → low sensitivity (DBD)
- spatial distribution of deposits differ between DBD and (MM)QTA

  → DBD – homogeneous distribution even in the discharge area

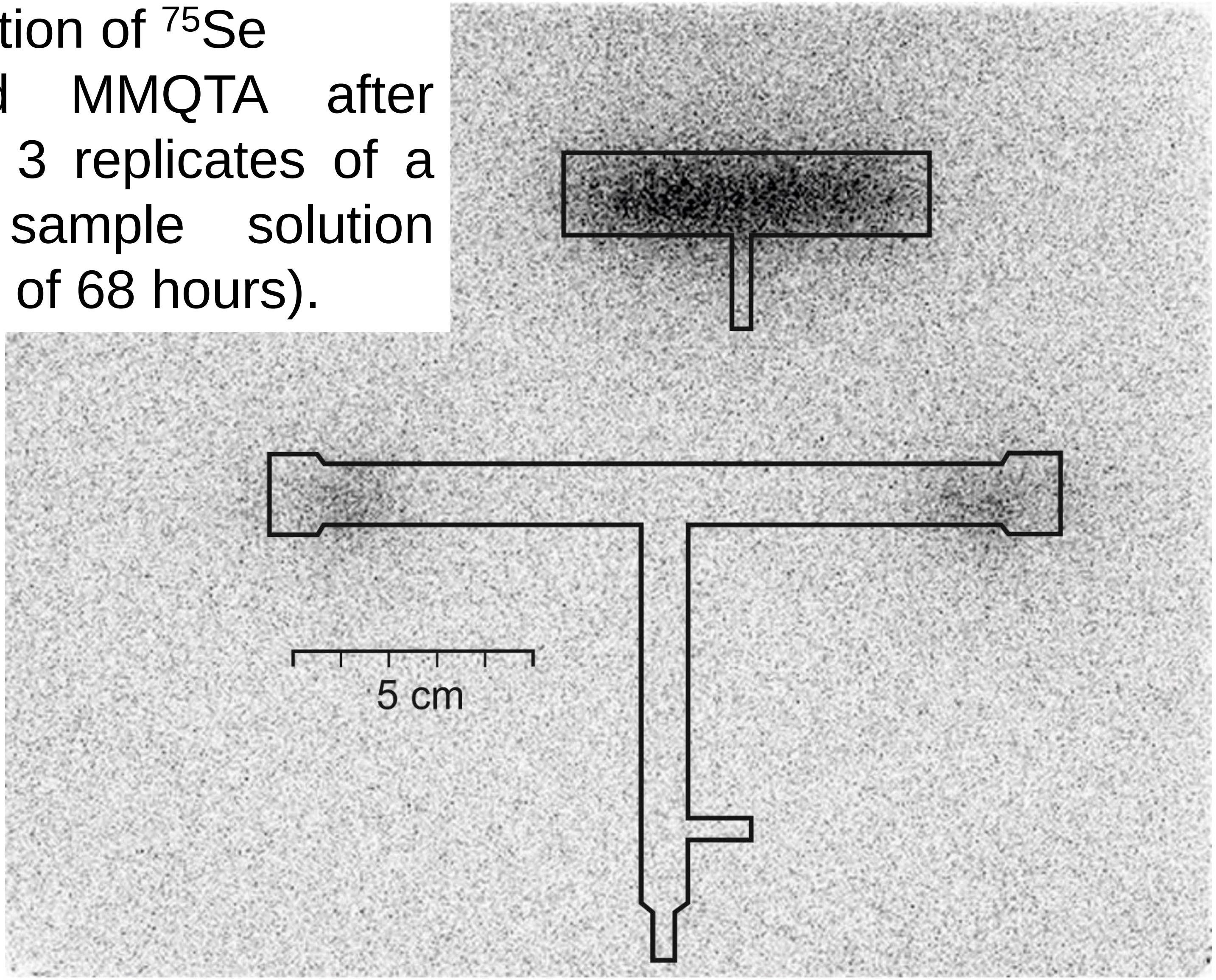
  → MMQTA – in the colder atomizer zones

J. Kratzer et al., Anal. Chim. Acta 1028 (2018) 11-21.

J. Kratzer et al., Anal. Chem. 88 (2016) 1804-1811.

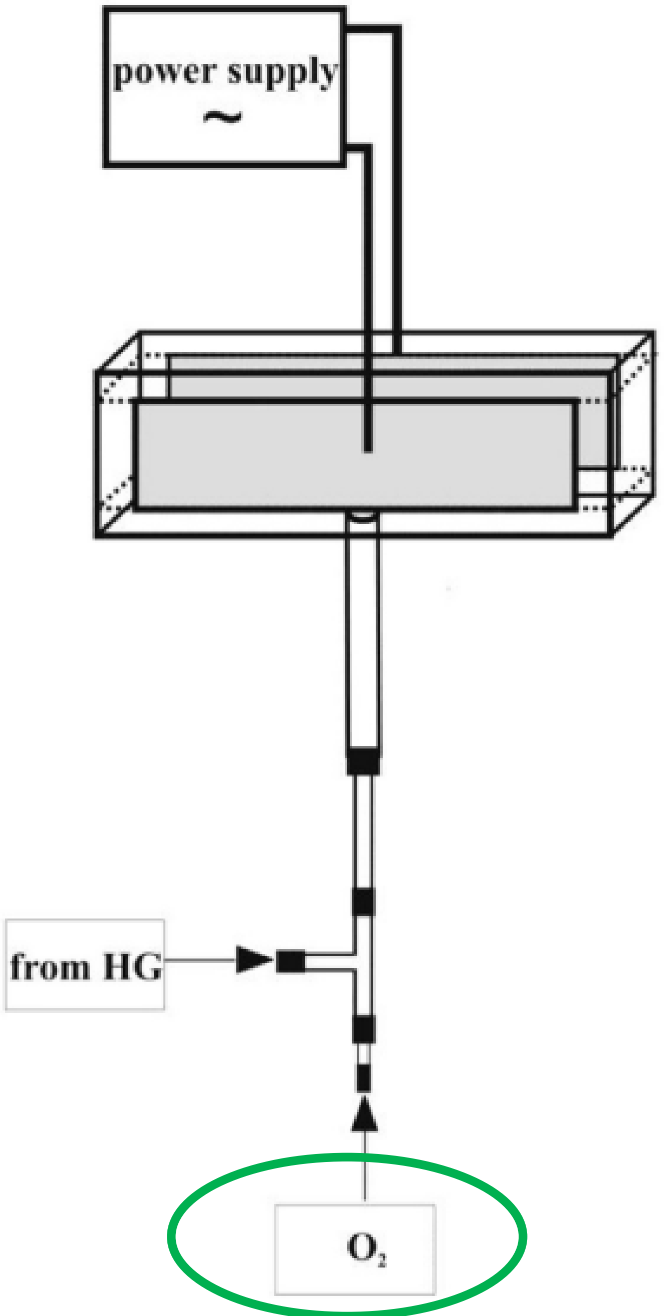
B. Baranová et al., Spectrochim. Acta B, accepted.

Spatial distribution of ^{75}Se in DBD and MMQTA after atomization of 3 replicates of a ^{75}Se tracer sample solution (exposure time of 68 hours).



J. Kratzer et al., Anal. Chim. Acta 1028 (2018) 11-21.

PRECONCENTRATION *IN-SITU* IN DBD



1) ANALYTE TRAPPING

Ar + O_2

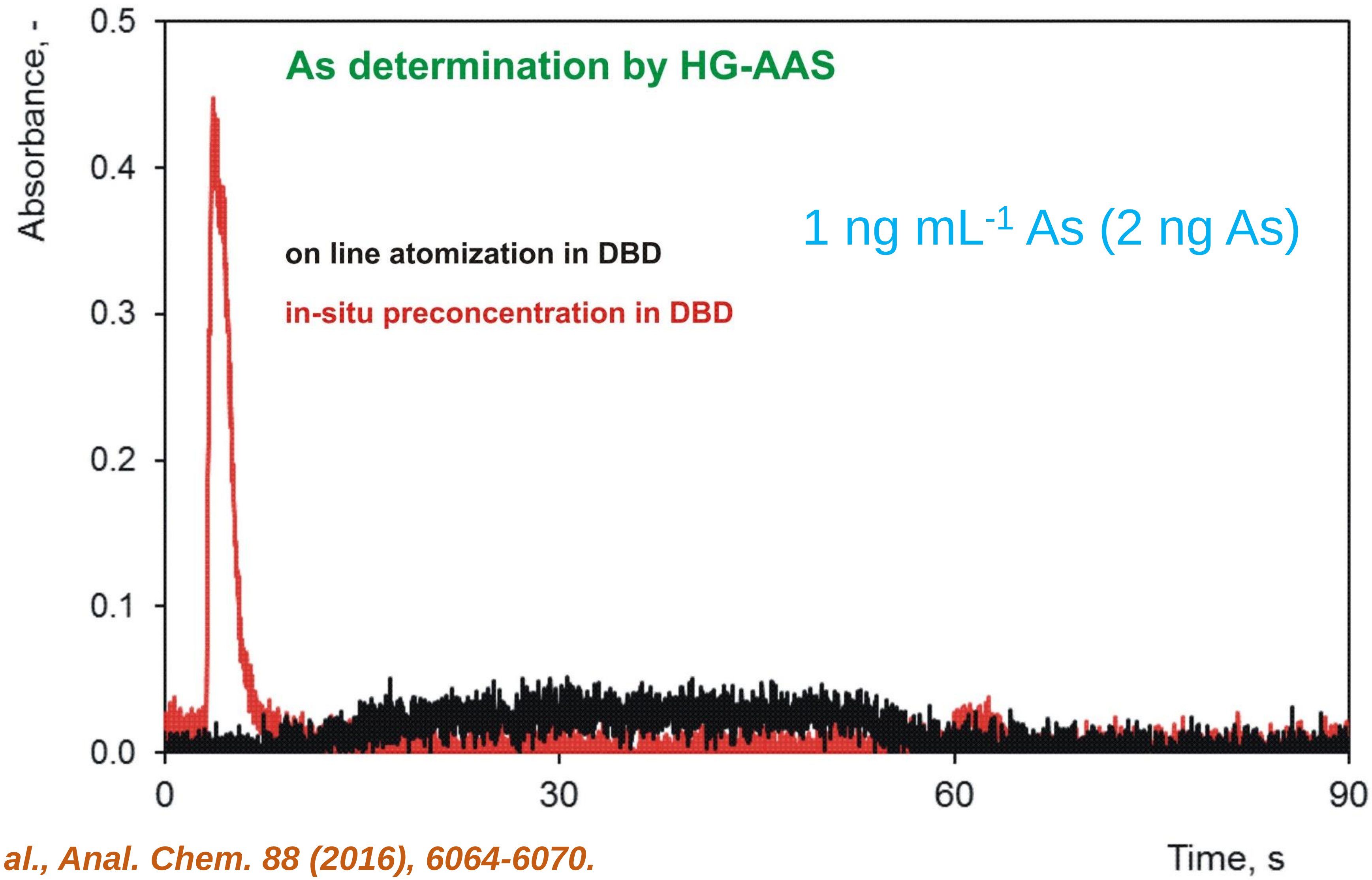
2) ANALYTE RELEASE

Ar + H_2 (blank)

No change in DBD HV / power settings

P. Novák et al., Anal. Chem. 88 (2016), 6064-6070.

IN-SITU PRECONCENTRATION IN DBD



P. Novák et al., Anal. Chem. 88 (2016), 6064-6070.

IN-SITU PRECONCENTRATION IN DBD

element	Preconcentration efficiency, %	LOD, ng mL^{-1}
As	100	0.01
Se	70	0.01
Sb	100	0.02
Te	51	-
Bi	60	-

P. Novák et al., Anal. Chem. 88 (2016), 6064-6070.

J. Kratzer et al., J. Anal. Atom. Spectrom. 34 (2019), 193-202

P. Zurynková et al., Anal. Chim. Acta 1010 (2018) 11-29.

K. Bufková et al., Spectrochim. Acta B 171 (2020) 105947.

J. Kratzer et al., Anal. Chem. 86 (2014), 9620-9625.

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- Novel hydride atomizers for AAS based on DBD plasma
- **VSG-based speciation analysis (Hg, Te, Ge, As)**
- VSG of mercury based on PMVG of Hg

A) selective VSG

VSG → detection *Te(IV) and Te(VI)*

B) post-column VSG

separation → VSG → detection *HPLC-VSG-ICP/MS*

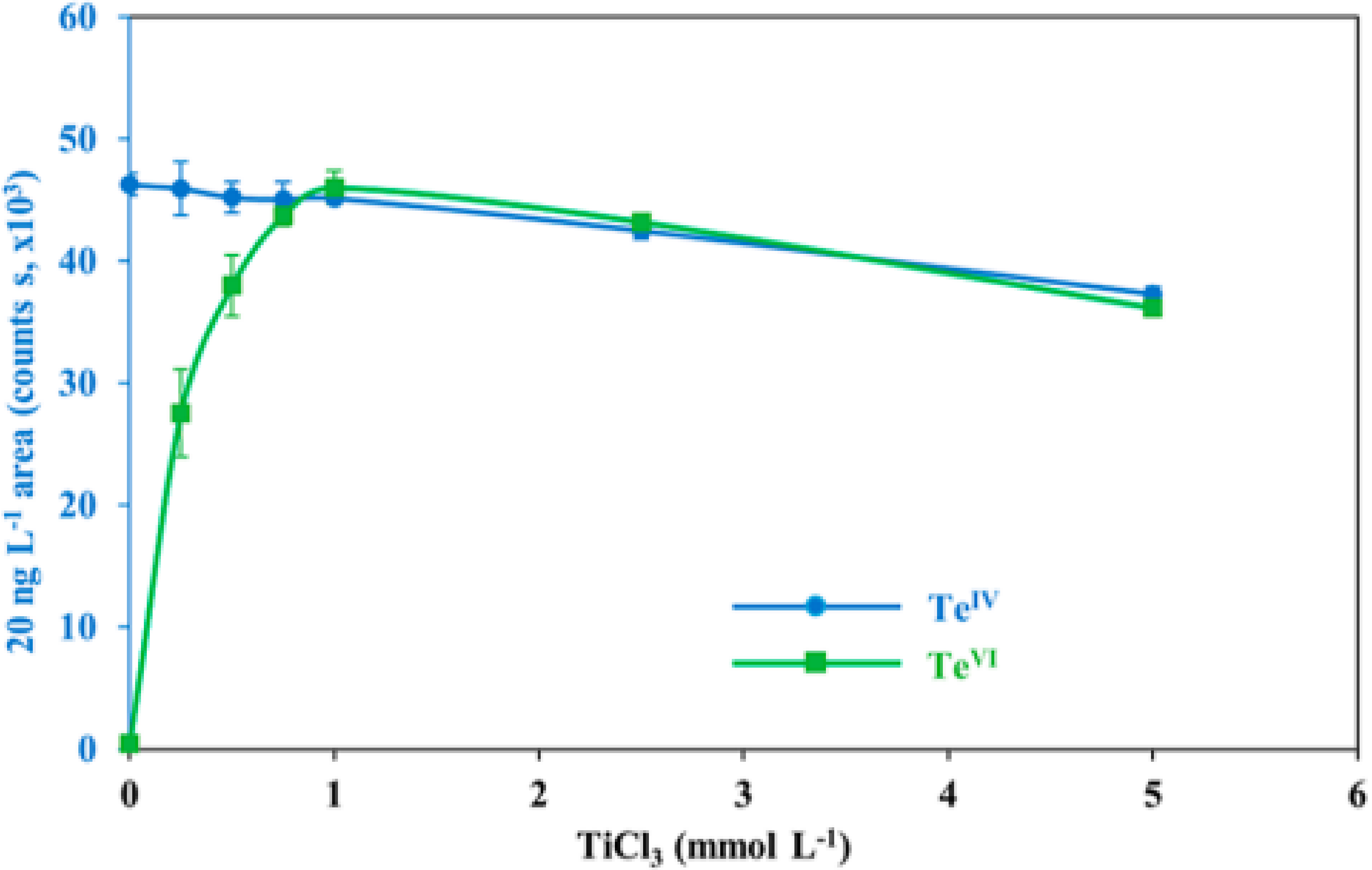
C) Generation of substituted volatile species

VSG → separation → detection *VSG-CT-ICP/MS*

selective VSG

VSG → detection

Te(IV) and Te(VI)



ICP-MS/MS

LOD: 2.3 pg L^{-1}

VSG-ICP-MS/MS

LOD: 0.07 ng L^{-1}

A. García-Figueroa et al., Anal. Chem. 94 (2022), 13995-14003.

A) selective VSG

VSG → detection

Te(IV) and Te(VI)

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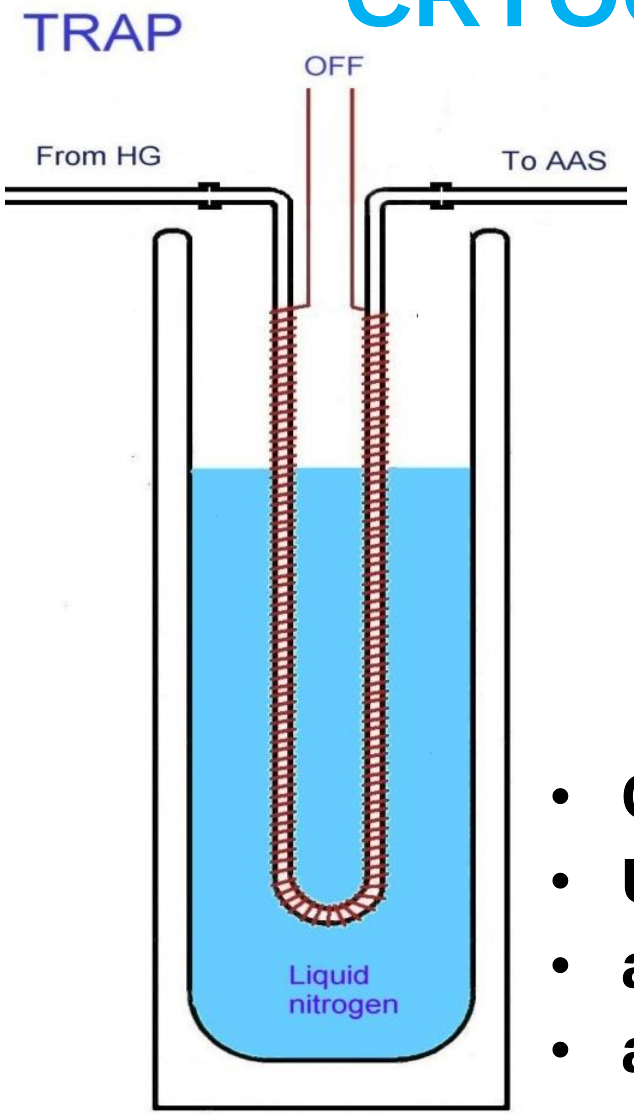
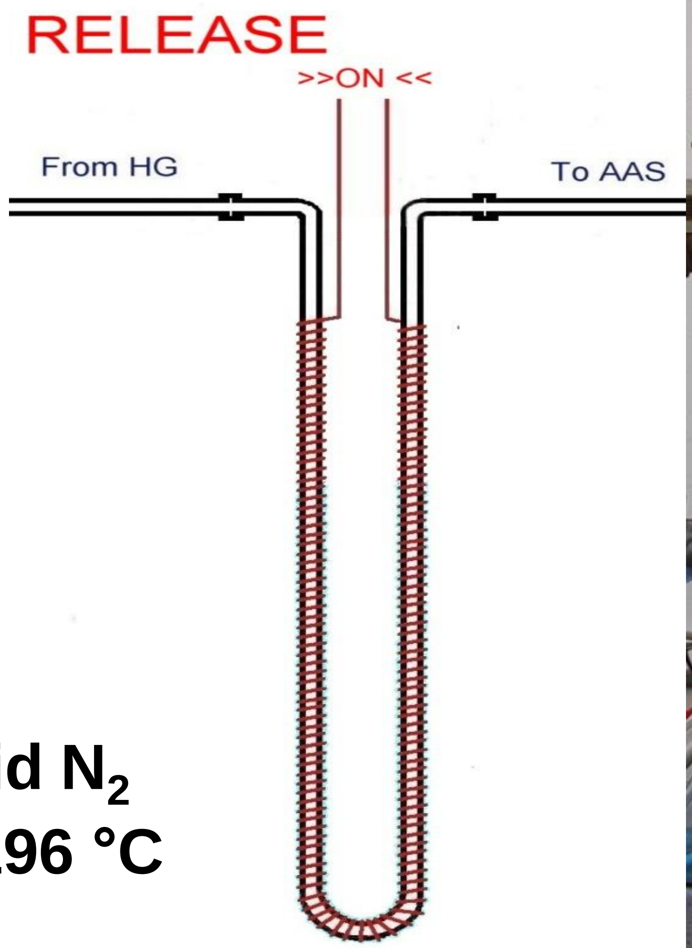
CRYOGENIC SEPARATION



trapping

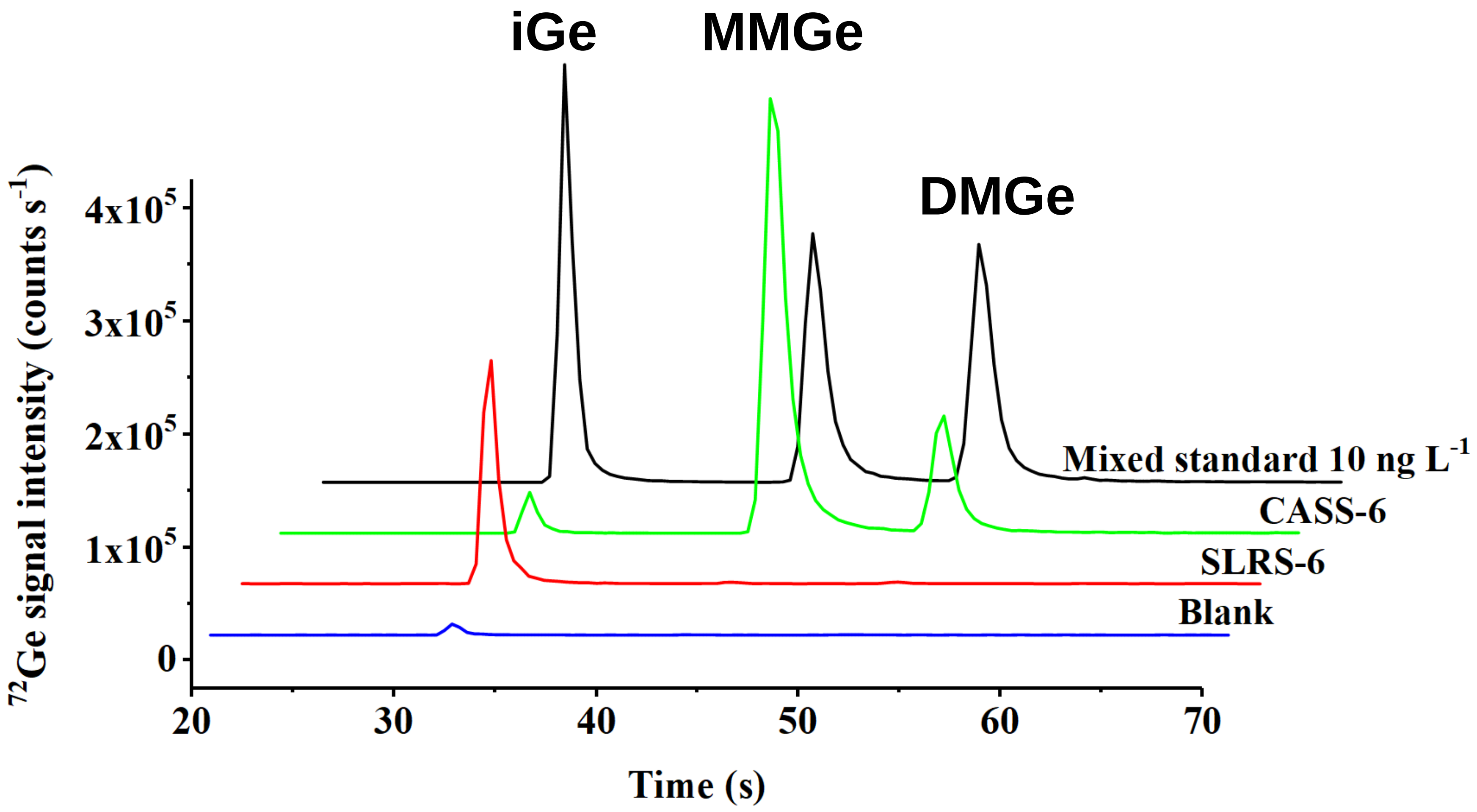
- Cryogenic trap (CT)
- U-tube immersed in liquid N_2
- all species retained @ -196 °C
- after heating the U-tube
- species separated according to their b.p.



release/separation

Speciation analysis of Ge – method development

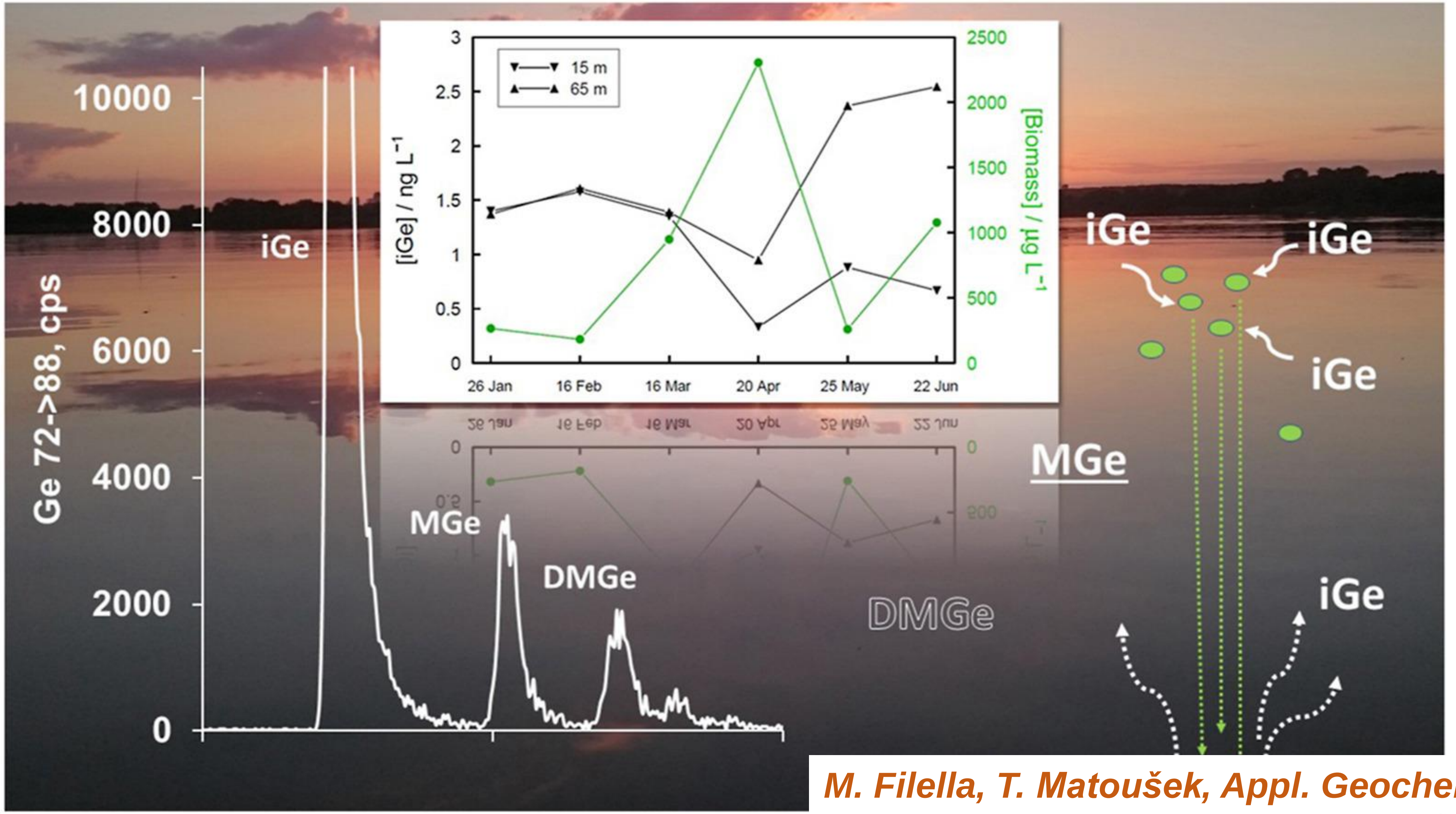
- VSG → separation → detection



A. García-Figueroa et al., Talanta 225 (2021), 121972.

Speciation analysis of Ge – applications

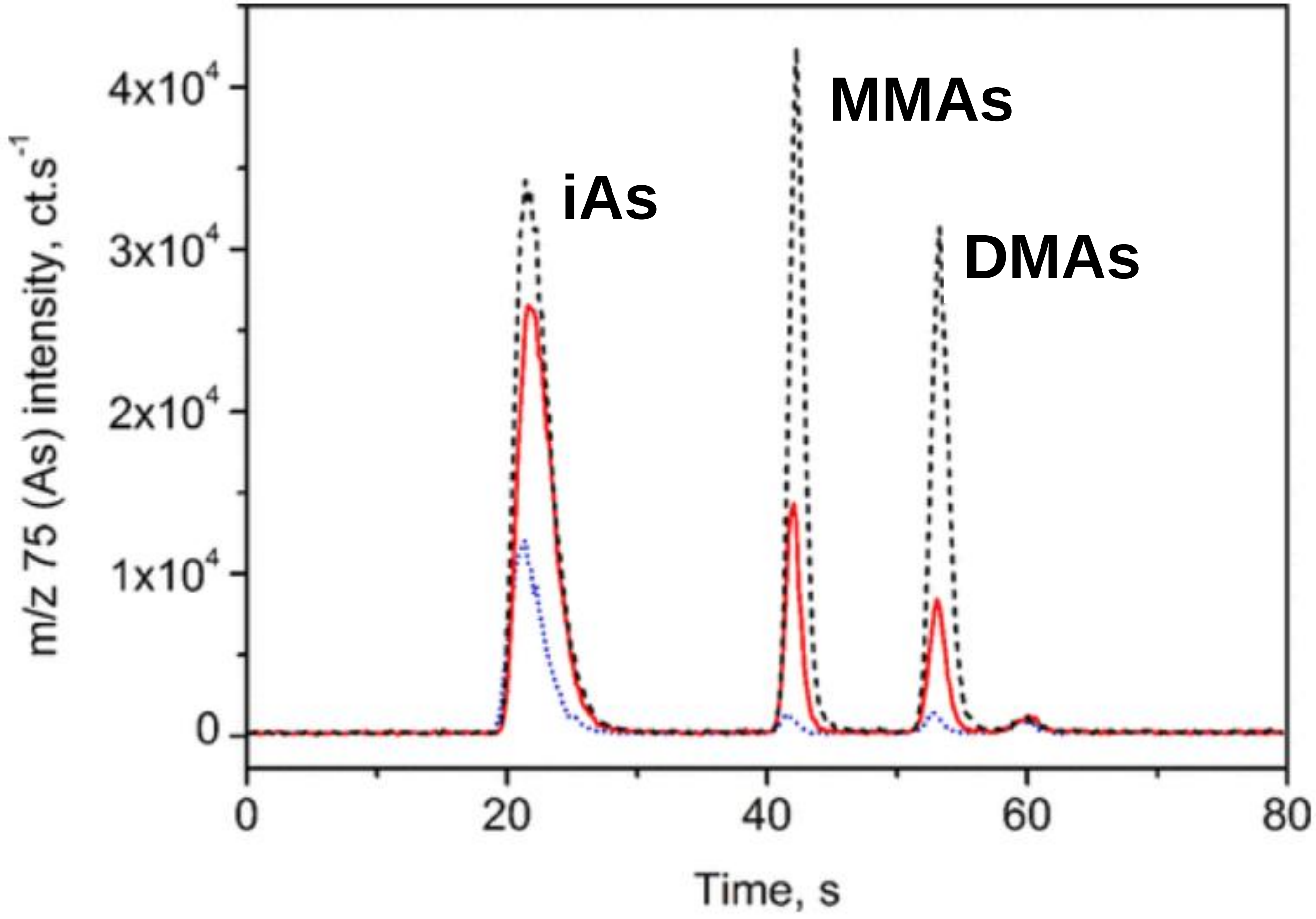
- **VSG → separation → detection**



M. Filella, T. Matoušek, Appl. Geochem. 143 (2022), 105352.

Speciation analysis of As – applications

- VSG → separation → detection



- in whole blood/plasma without extraction

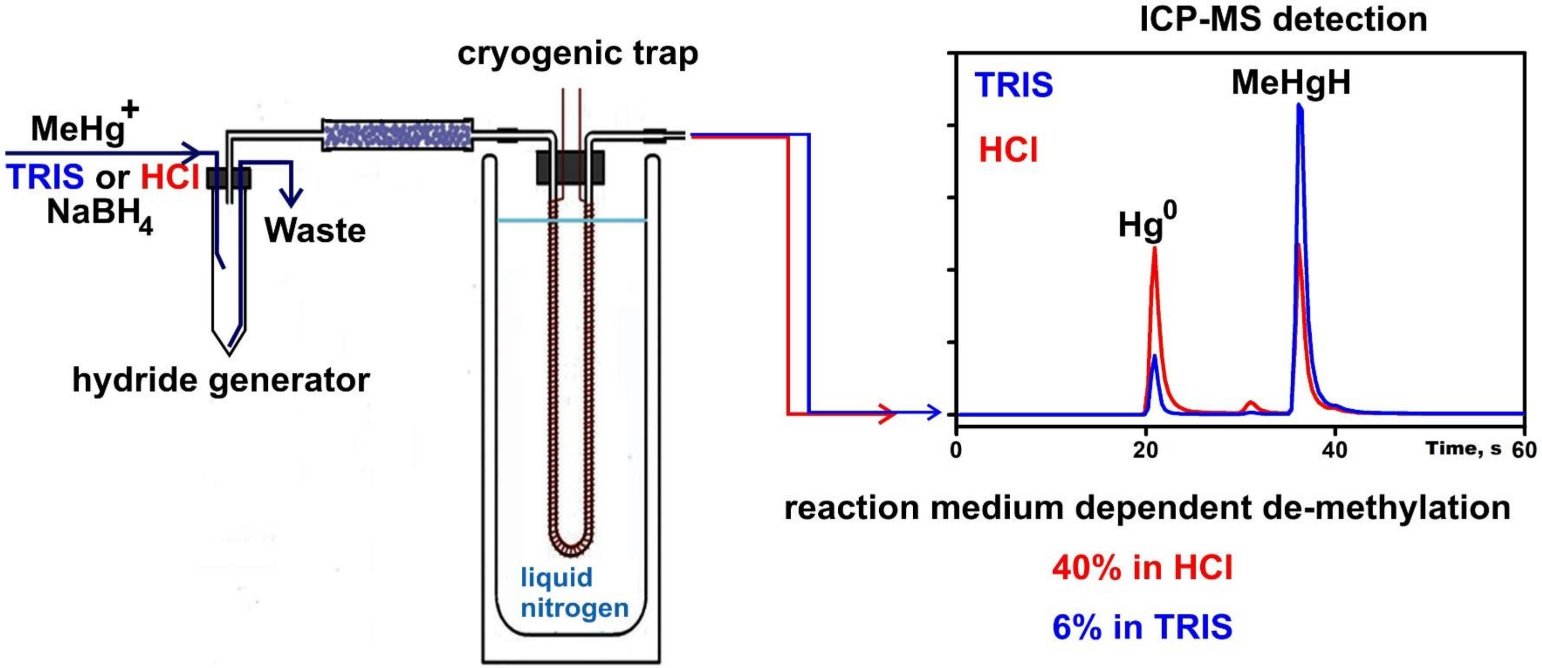
- 50-100 µl samples
- LOD ~ pg ml^{-1}
- normal levels of exposure

T. Matoušek et al., Anal. Chem. 89 (2017), 9633-9637.

Generation of alkyl-/aryl-substituted volatile species

- VSG → separation → detection
- VSG from HCl and TRIS buffer media
- cryogenic trap (CT) used for separation

- $Hg^{2+} \rightarrow Hg^0$
- $MeHg^+ \rightarrow MeHgH$
- $EtHg^+ \rightarrow EtHgH$
- $PhHg^+ \rightarrow PhHgH$



M. Migašová et al., Anal. Chim. Acta 1119 (2020), 68-76.

- **decomposition of substituted species during VSG step !!!**

- **more pronounced in HCl than TRIS buffer media**

quantification of fraction decomposed to Hg^0 (%)

	HCl	**TRIS**
MeHgH	41	6
EtHgH	77	28
PhHgH	94	99

M. Migašová et al., Anal. Chim. Acta 1119 (2020), 68-76.

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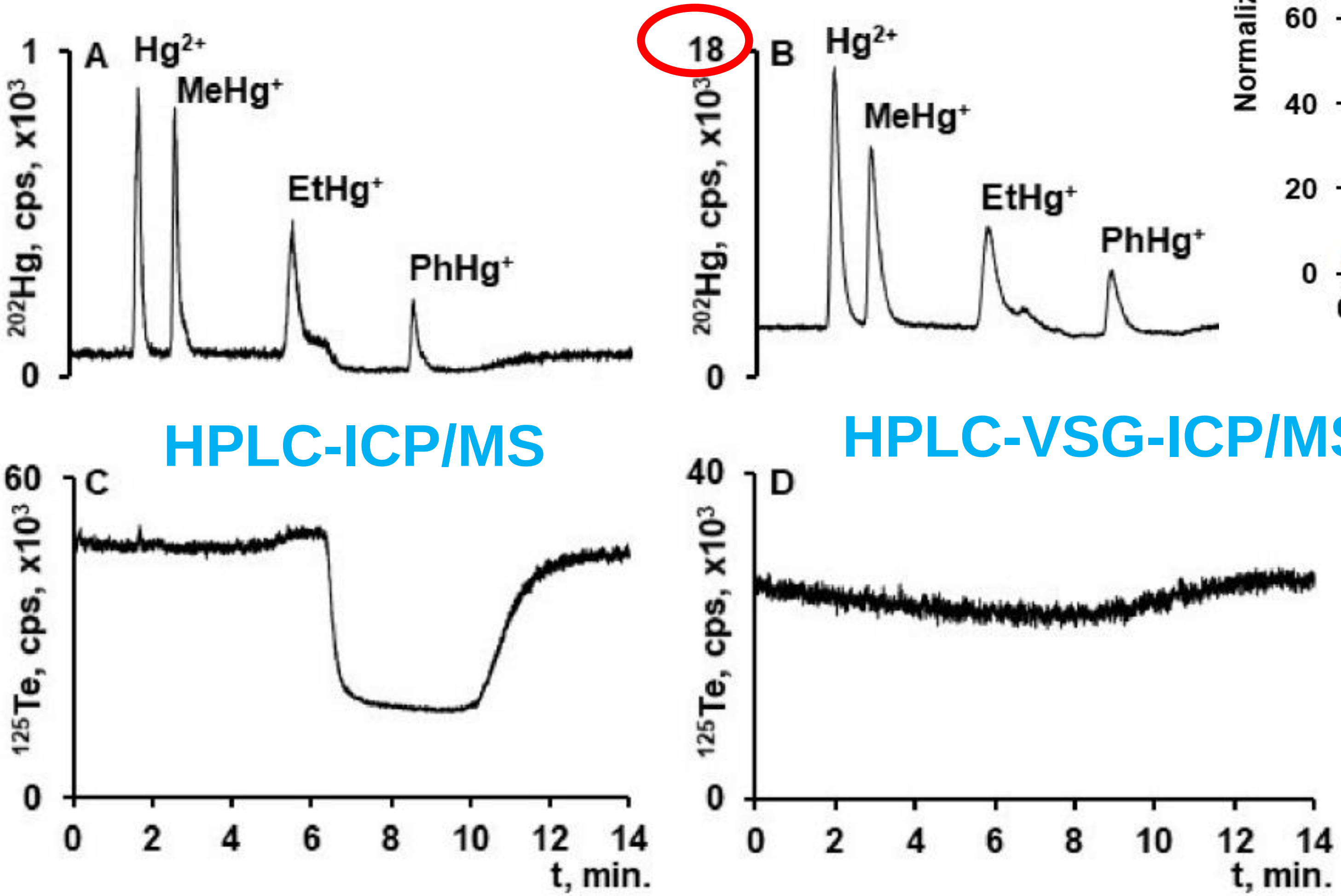
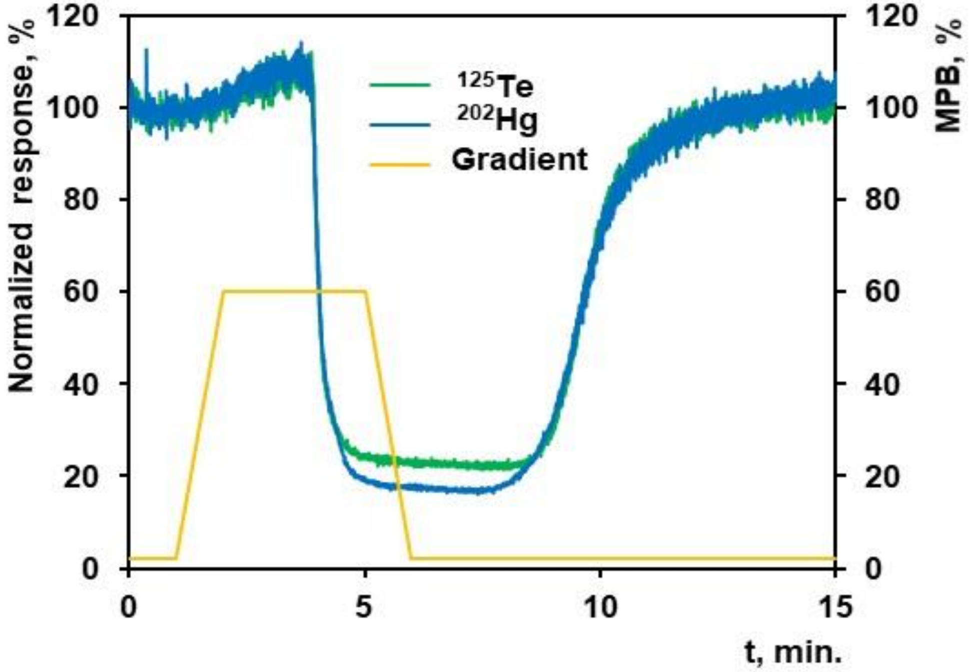
- separation → VSG → detection





HPLC-VSG-ICP/MS

mobile phase matrix elimination

constant IS response

increased ICP/MS sensitivity

Fig. 3. Chromatograms of mercury species (^{202}Hg) mixed standard solution of Hg^{2+}, $MeHg^{+}$, $EtHg^{+}$ and $PhHg^{+}$ containing 1 μg L^{-1} (as Hg) of each species, obtained without (A) and with postcolumn VSG step (B). The IS signal (^{125}Te signal) obtained without (C) and with postcolumn VSG step (D).

I. Petry-Podgórska et al., Microchem. J. 170 (2021), 106606.

Post-column VSG: separation → VSG → detection

Analytical figures of merit found for HPLC-ICP/MS and HPLC-VSG-ICP/MS

Species	Slope Cts L μg^{-1}	LOD ($ng\ L^{-1}$)
HPLC-ICP-MS		
Hg^{2+}	10 213	15
$MeHg^{+}$	9 957	15
$EtHg^{+}$	10 120	17
$PhHg^{+}$	3 499	26
HPLC-VSG-ICP-MS		
Hg^{2+}	398 430	3
$MeHg^{+}$	351 989	2
$EtHg^{+}$	336 402	4
$PhHg^{+}$	178 399	6

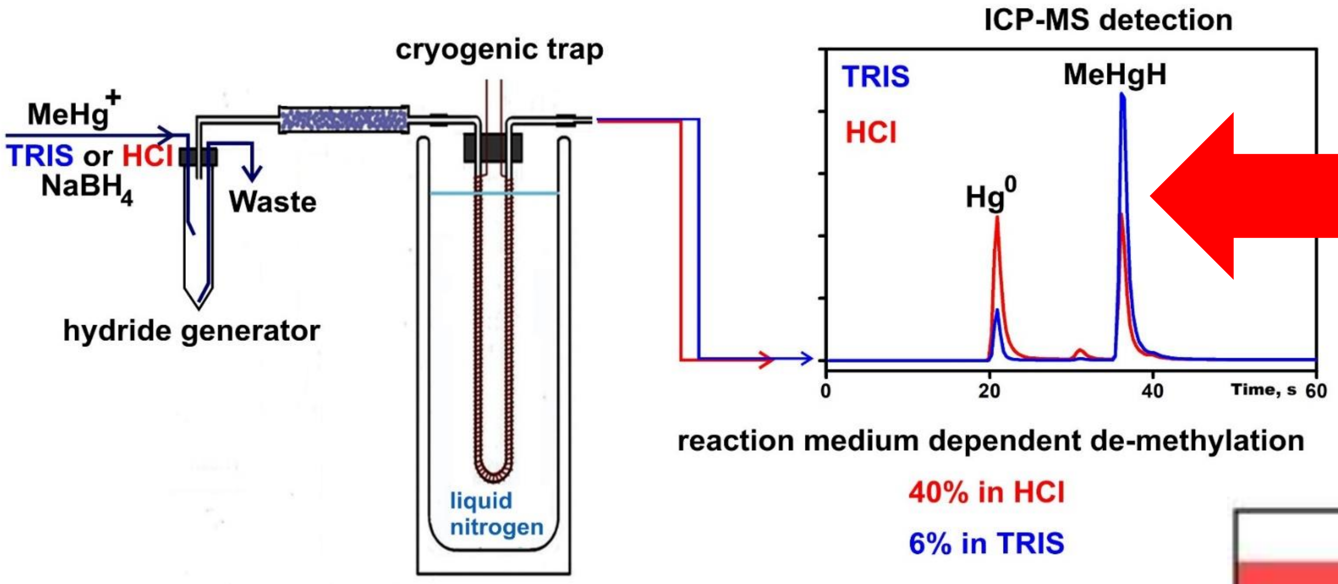
HPLC-VSG-ICP/MS

Sensitivity increased 30-40 times

LOD improved 3-7 times

I. Petry-Podgórska et al., Microchem. J. 170 (2021), 106606.

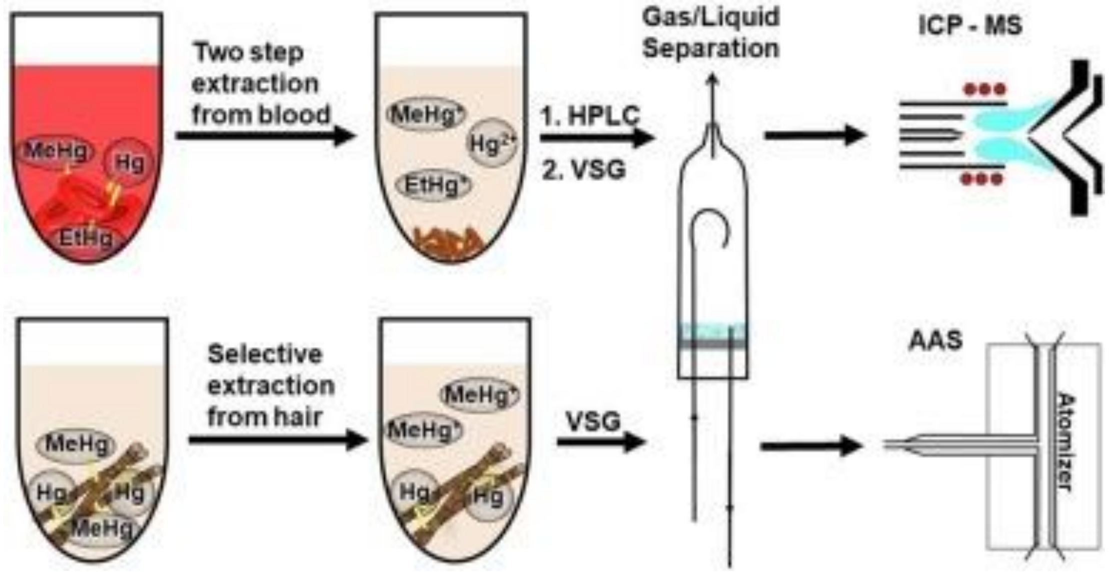
VSG-based speciation analysis of Hg



Generation of substituted VS

analytical artifacts

M. Migašová et al., Anal. Chim. Acta 1119 (2020), 68-76.



post-column VSG

reliable approach

I. Petry-Podgórska et al., Microchem. J. 170 (2021), 106606.

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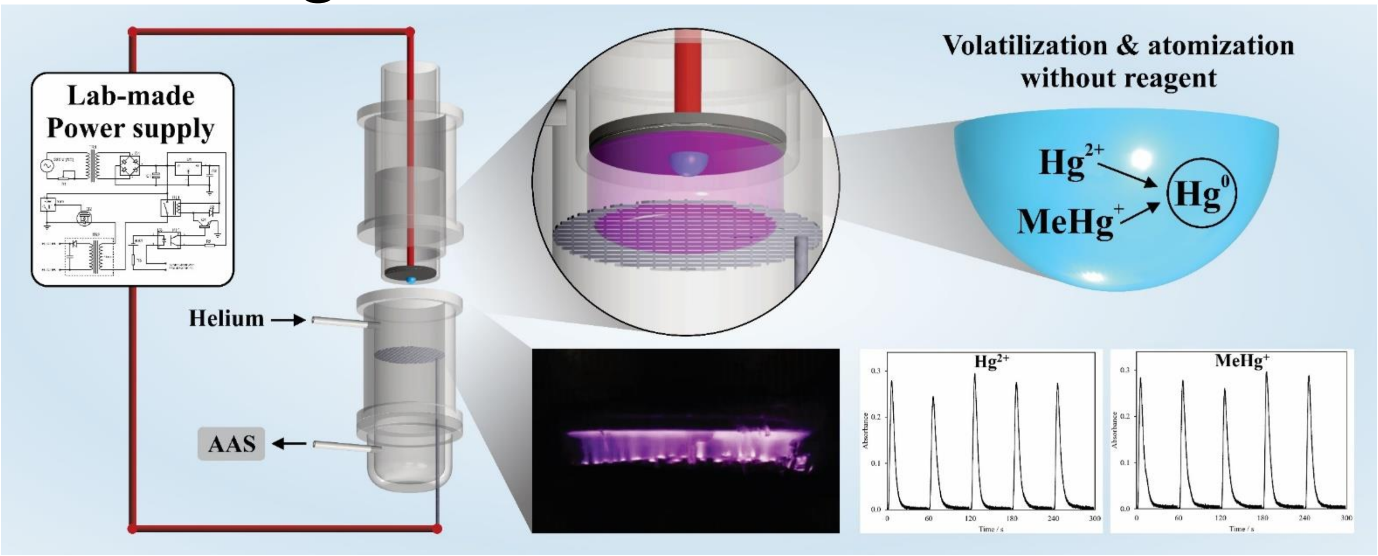
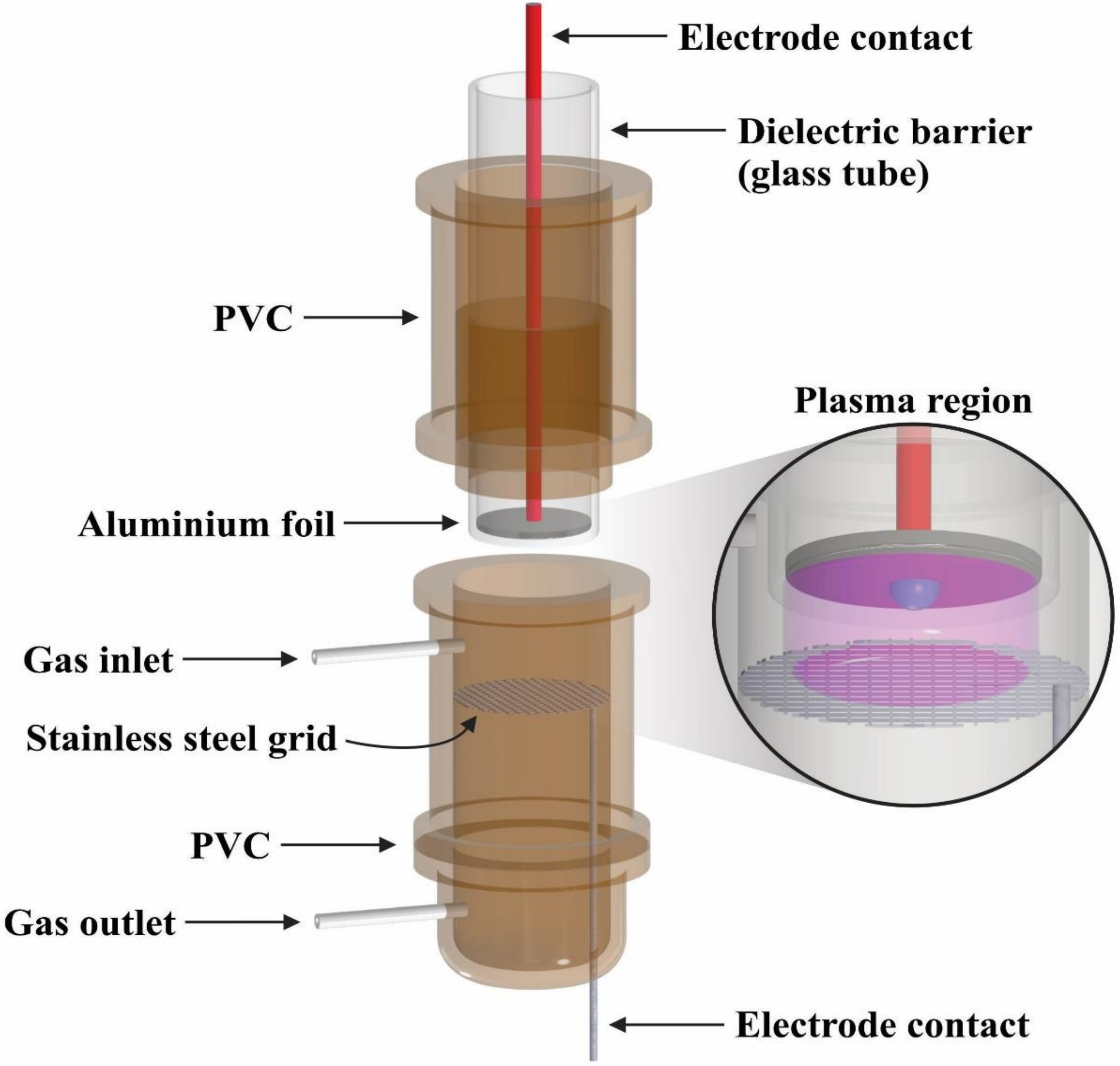


G. da Silva Coelho Junior et al., Spectrochim. Acta B, submitted.



laboratory made DBD reactor

AAS detector

QTA atomizer @ ambient temperature

150 mL min^{-1} He

Samples – droplets (2 μL)

Hg^{2+}

$MeHg^{+}$

38 kV, 23 W, 40 kHz, 60% duty cycle

laboratory made power supply source

- **PMVG efficiency quantified**
  - **Hg^{2+}** **87 ± 8 %**
  - **$MeHg^{+}$** **91 ± 10 %**
- **both Hg species volatilized and atomized in the DBD reactor**
- **sensitivity of PMVG comparable with CVG**
- **LOD 200 pg Hg**

CONCLUSIONS

- **VSG of Cd**
  - **promising approach, 60% efficiency**
- **novel DBD hydride atomizers**
  - **can compete with QTAs (As, Se, Te)**
  - ***in-situ* preconcentration feasible**
- **VSG for speciation analysis**
  - **postcolumn VSG – reliable approach**
  - **generation of substituted VS – artifacts due to species decomposition (Hg)**
    - **reliable approach for As and Ge**
- **PMVG of Hg**
  - **high introduction efficiency**
  - **good choice for volume-limited samples**

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