Charge transfer matrix effects in inductively coupled plasma mass spectrometry: the more the better

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ICP-MS: fundamentals

Applications

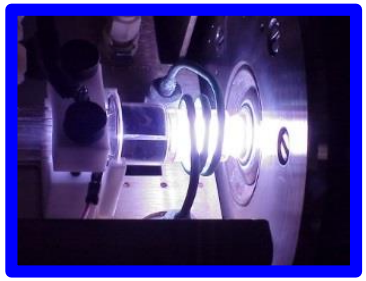
Environmental

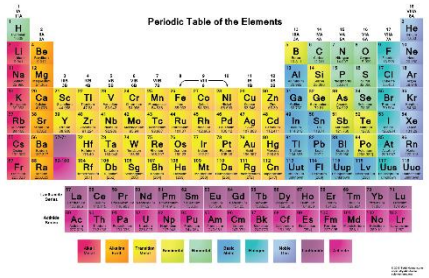
Industry

Foods

Biosciences

ICP-MS

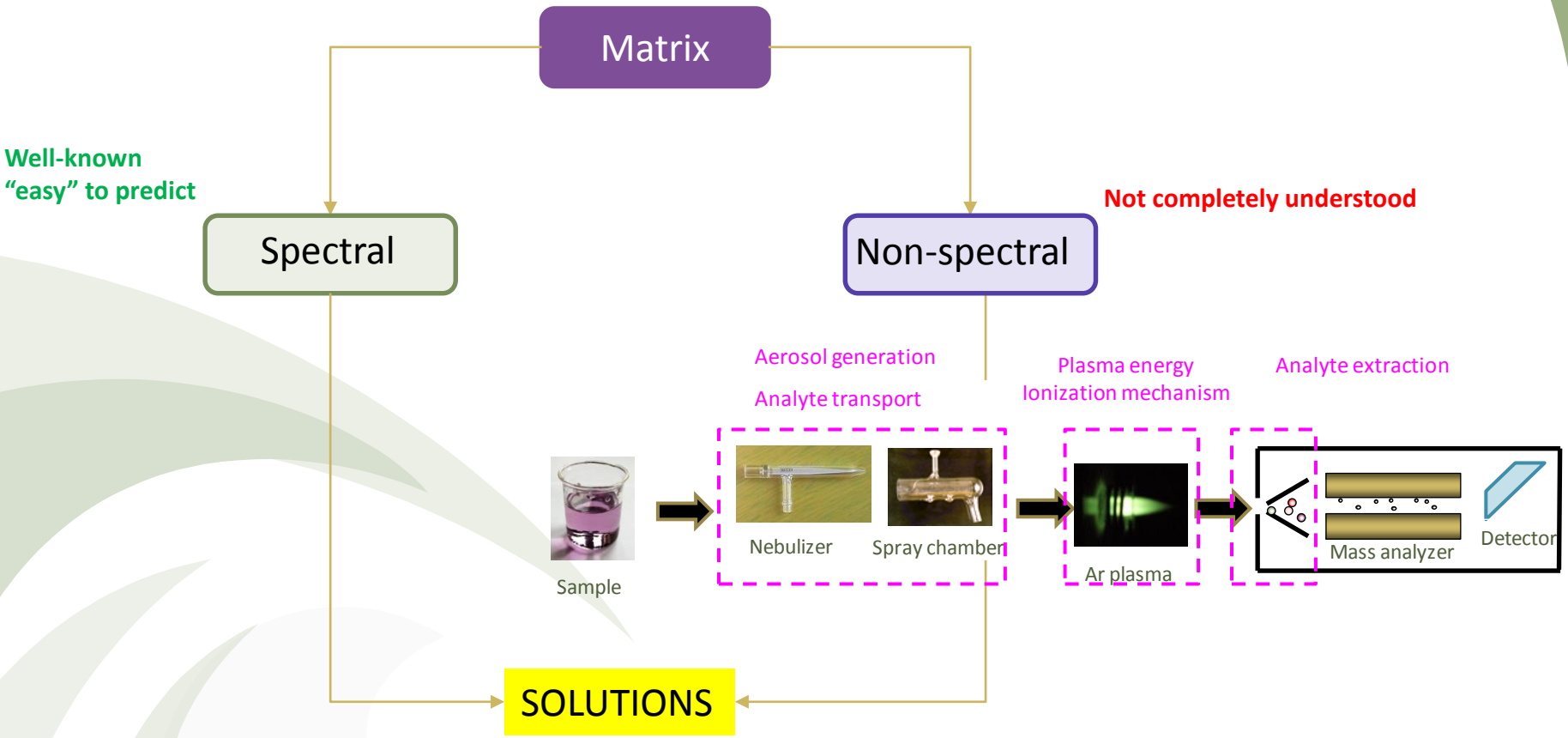




Matrix

- **Accuracy and precision**
- **Limits of detection (<µg L^{-1})**
- Multi-element capabilities
- Wide dynamic range
- Isotopic information
- Hyphenated techniques

ICP-MS: interferences



- Instrumentation (HR, CCT, etc.)
- Mathematical equations
- Experimental conditions
- Sample introduction system
- Sample pretreatment
- Quantification methodology (e.g. IS)

ICP-MS: interferences

DRAWBACKS

Matrix effects

BENEFITS

- Lower analyte transport
- Lower plasma energy
- Changes atom-ion equilibrium
- Lower analyte extraction
- High background signals
- Carbon/salt deposits

↓ Sensitivity
↓ Precision
↑ LOD

- **Higher analyte transport**

  Organics: (i) lower surface tension

  (ii) higher volatility

- **Lower background**

  Propanol: lower Ar_2^+ and $ArCl^+$

- **Higher ionization**

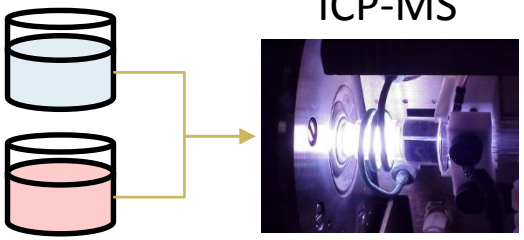
  Charge transfer reactions

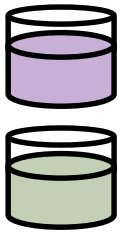
↑ Sensitivity
↑ Precision
↓ LOD

Charge transfer reactions in ICP-MS

Analyte:100 ppb
Nitric acid 1%

Analyte:100 ppb
Glycerol (Carbon 20 g L^{-1})



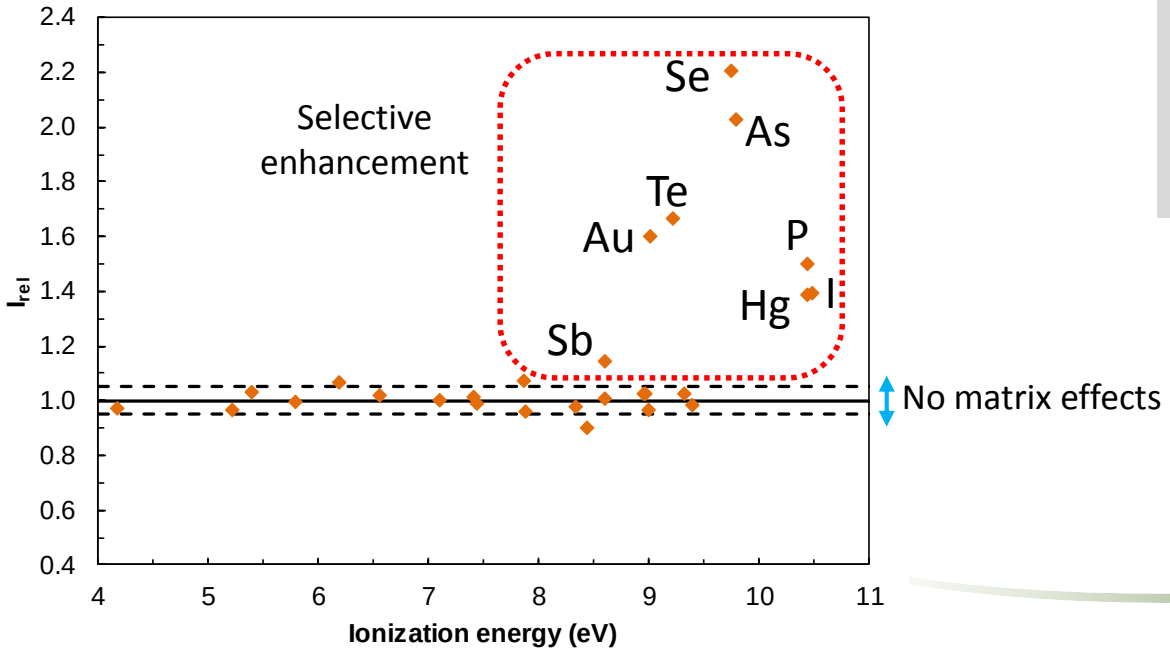


H_2SO_4
(Sulfur 20 g L^{-1})

H_3PO_4
(Phosphorous 20 g L^{-1})

Similar findings

$$I_{rel} = \frac{I_{Carbon}}{I_{HNO_3}}$$



Signal enhancement origin?

☒ Aerosol generation
☒ Aerosol transport
☒ Plasma temperature
☒ Ion extraction
☑ **Ionization mechanism?**

Grindlay et al. Spectrochimica Acta Part B 86 (2013) 42–49

García-Poyo et al, Spectrochimica Acta Part B 105 (2015) 71–76

Grindlay et al. Spectrochimica Acta Part B 115 (2016) 8–15

Charge transfer reactions: fundamentals

Analyte ionization mechanisms in Ar-plasmas

- Electron-impact ionization

  $M + e^- \rightarrow M^+ + e^-$

- Penning ionization:

  $Ar^* + M \rightarrow Ar + (M^+)^* + e^-$

- **Charge transfer reaction:**

  $Ar^+ + M \rightarrow Ar + (M^+)^* + \Delta E$

Ar^+: argón ion Ar: argon atom ΔE: energy deffect
M: analyte atom $(M^+)^*$: excited analyte ion

Reaction requeriments

- Energy defect
- Spin conservation

- **Matrix-based charge transfer reactions:**

  Concomitant ionization: C^+, S^+ and P^+

  $C^+ + M \rightarrow C + (M^+)^* + \Delta E$
  $S^+ + M \rightarrow S + (M^+)^* + \Delta E$
  $P^+ + M \rightarrow P + (M^+)^* + \Delta E$

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Charge transfer reactions: fundamentals

Matrix-element dependent!!!!!

Carbon

P, As, Se, Sb, Te, I, Au, Hg

						He
	B	C	N	O	F	Ne
	Al	Si	**P**	S	Cl	Ar
Ni	Cu	Zn	Ga	Ge	**As**	**Se**	Br	Kr
Pd	Ag	Cd	In	Sn	**Sb**	**Te**	**I**	Xe
Pt	**Au**	**Hg**	Tl	Pb	Bi	Po	At	Rd
Ds	Rg	Cn	Uut	Fi	Uup	Lv	Uus	Uuo

Sulfur

P, As, Se, Te, I

						He
	B	C	N	O	F	Ne
	Al	Si	**P**	S	Cl	Ar
Ni	Cu	Zn	Ga	Ge	**As**	**Se**	Br	Kr
Pd	Ag	Cd	In	Sn	**Sb**	**Te**	**I**	Xe
Pt	**Au**	**Hg**	Tl	Pb	Bi	Po	At	Rd
Ds	Rg	Cn	Uut	Fi	Uup	Lv	Uus	Uuo

Phosphorous

As, Se, Sb, Te

						He
	B	C	N	O	F	Ne
	Al	Si	P	S	Cl	Ar
Ni	Cu	Zn	Ga	Ge	**As**	**Se**	Br	Kr
Pd	Ag	Cd	In	Sn	**Sb**	**Te**	I	Xe
Pt	**Au**	**Hg**	Tl	Pb	Bi	Po	At	Rd
Ds	Rg	Cn	Uut	Fi	Uup	Lv	Uus	Uuo

Significant for poorly ionized elements

Element	Ionization degree (%)	Element	Ionization degree (%)
P	33	Te	66
As	52	I	29
Se	33	Au	51
Sb	78	Hg	38

Unexpected behavior for some elements with high IP

Os, Ir, Pt, etc. → reaction kinetics?

Grindlay et al. Spectrochimica Acta Part B 86 (2013) 42–49

García-Poyo et al, Spectrochimica Acta Part B 105 (2015) 71–76

Grindlay et al. Spectrochimica Acta Part B 115 (2016) 8–15

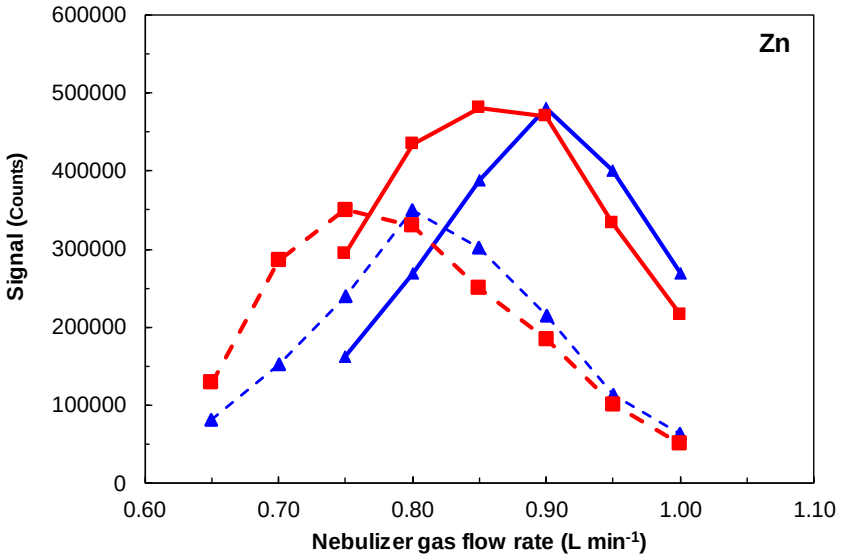
Charge transfer reactions in ICP-MS

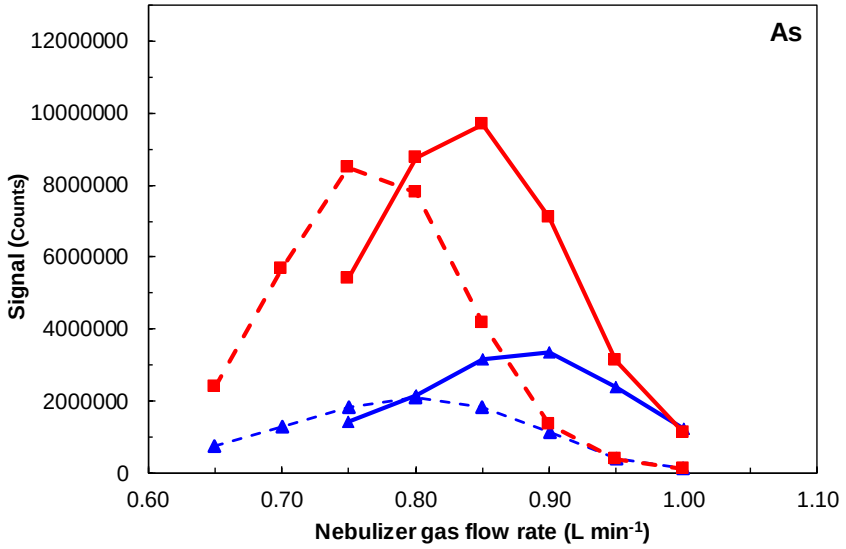
Influence of experimental conditions: R.f. power and nebulizer gas flow

— r.f. power 1400 W, carbon 20 g L^{-1} - - - r.f. power 1100 W, carbon 20 g L^{-1}

— r.f. power 1400 W, nitric acid 1% - - - r.f. power 1100 W, nitric acid 1%

Q_l 0.6 mL min^{-1}





- **Changes on the optimum Q_g by carbon (cooling effect)**
- **Signal enhancement for As when increasing r.f. power or reducing Qg**

$$C^+ + M \rightarrow C + (M^+)^* + \Delta E$$

Robust conditions increase concomitant ionization (higher C^+ concentration)

Grindlay et al. Spectrochimica Acta Part B 86 (2013) 42–49

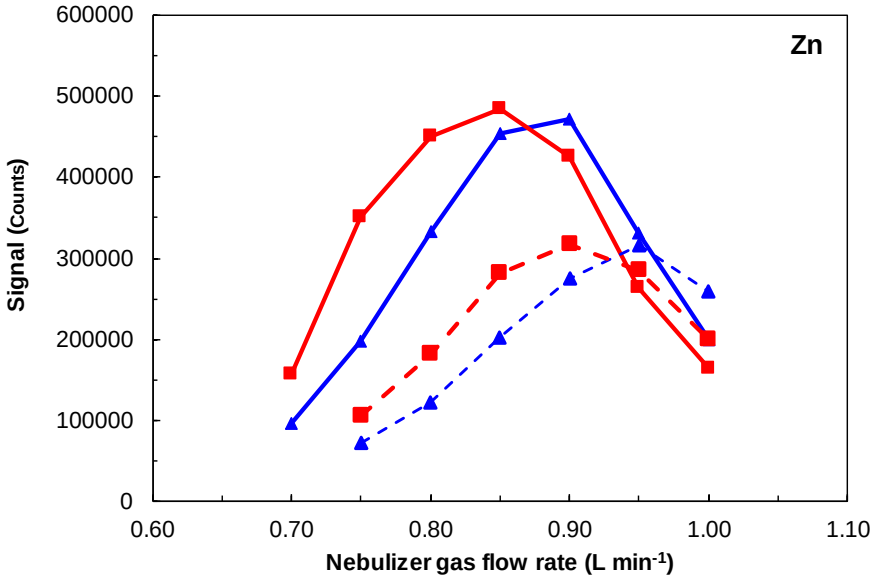
Charge transfer reactions in ICP-MS

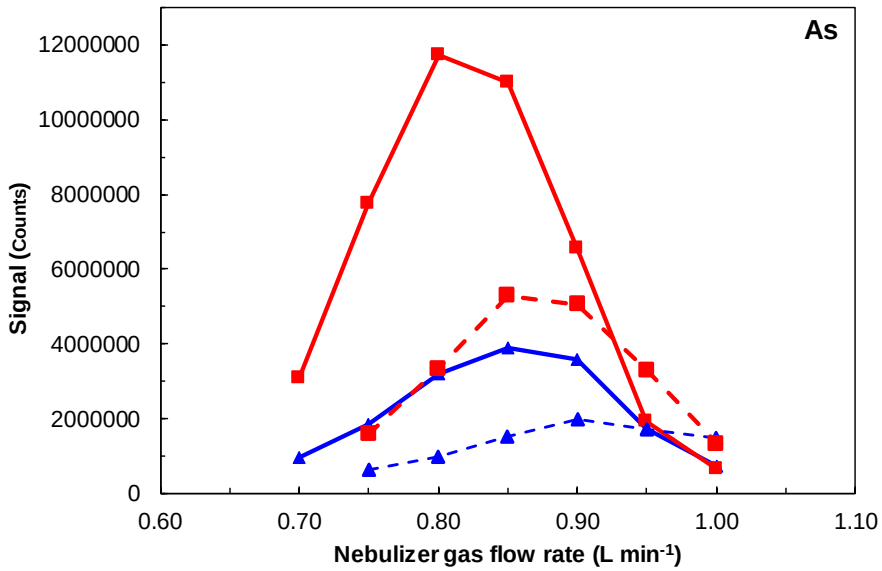
Influence of experimental conditions: sample uptake rate and nebulizer gas flow

— Q_l 1.0 mL min^{-1}, carbon 20 g L^{-1} - - - Q_l 1.0 mL min^{-1}, carbon 20 g L^{-1}

— Q_l 1.0 mL min^{-1}, nitric acid - - - Q_l 1.0 mL min^{-1}, nitric acid

r.f. power 1400 W





- **Changes on the optimum Q_g by carbon (cooling effect)**
- **Signal enhancement for As when increasing Ql or reducing Qg**

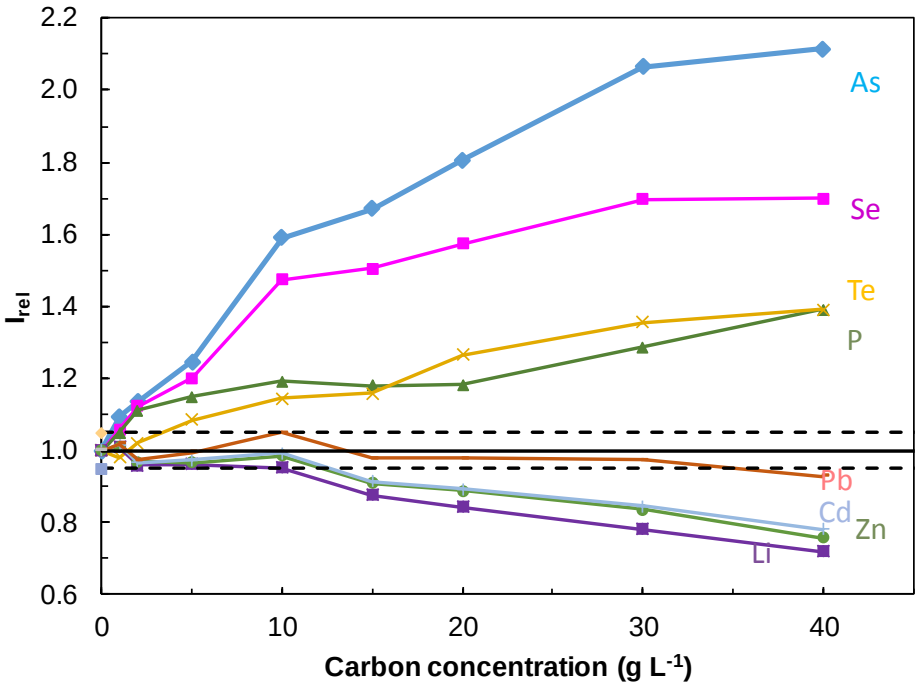
$$C^+ + M \rightarrow C + (M^+)^* + \Delta E$$

Higher Q_l increases concomitant concentration in the plasma (higher C^+ concentration)

Grindlay et al. Spectrochimica Acta Part B 86 (2013) 42–49

Charge transfer reactions in ICP-MS

Influence of experimental conditions: matrix concentration and type



Experimental conditions: glicerol (carbon), Q_l 1,0 mL min^{-1}; Q_g: 0.85 L min^{-1}; r.f. power: 1400 W.

$$C^+ + M \rightarrow C + (M^+)^* + \Delta E$$

Higher matrix content increases concomitant concentration in the plasma (higher C^+ concentration)

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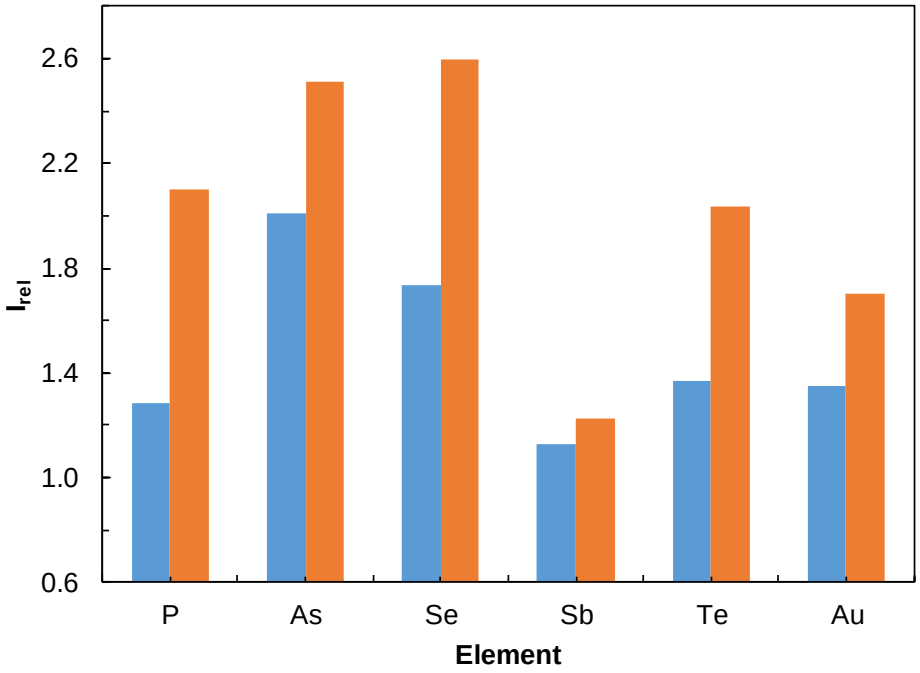
Charge transfer reactions in ICP-MS

Influence of experimental conditions: sample introduction system



Cyclonic spray chamber

Single pass spray chamber

Carbon source: glycerol; carbon concentration 20 g L^{-1}; r.f. power: 1400W; Q_i: 0.2 mL min^{-1}; Qg 0.95 L min^{-1} (cyclonic spray chamber); 0.85 L min^{-1} (single pass spray chamber)

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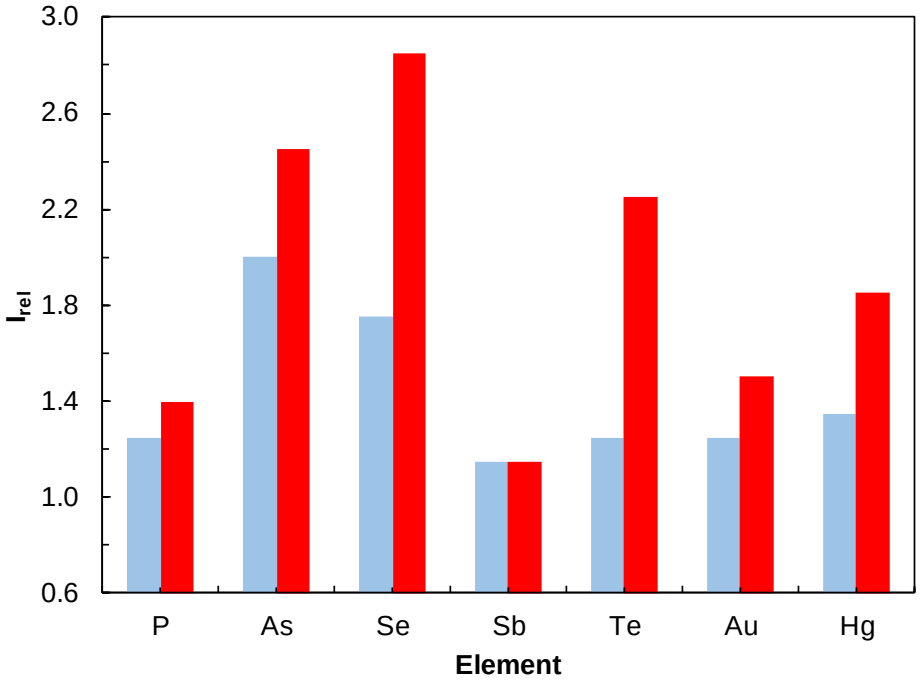
Charge transfer reactions in ICP-MS

Influence of experimental conditions: mass spectrometer design



Glycerol (Carbon concentration 20 g L^{-1}). Q-ICP-MS: Q_l 1,0 mL min^{-1}; Q_g: 1.10 L min^{-1}; r.f. power: 1300 W; cyclonic spray chamber. SF-ICP-MS: Q_l 0.2 mL min^{-1}; Q_g: 0.87 L min^{-1}; r.f. power: 1300 W; mini-cyclonic spray chamber

Grindlay et al. Spectrochimica Acta Part B 86 (2013) 42–49

Charge transfer matrix effects in ICP-MS

Is it possible to exploit them?

How to exploit charge transfer-based matrix effects in ICP-MS

1. **Introduce some carbon- sulfur- or phosphorous- containing compounds in the plasma:**

   a. **During the sample preparation step**
   b. **Eluent in HPLC**
   c. **Gas addition (methane, carbon dioxide, etc.): mixed plasmas**

Concomitant	Matrix type
Carbon	Non-volatile matrix (e.g. sugars, ..) Volatile matrix (e.g. methanol, … Gas addition (e.g. methane, …)
Sulfur	H_2SO_4
Phosphorous	H_3PO_4

How to exploit charge transfer-based matrix effects in ICP-MS

1. **Introduce some carbon- sulfur- or phosphorous- containing compounds in the plasma:**

Element	Concomitant
P	C
As	C
Se	C
Sb	C / P
Te	S
I	C
Au	C
Hg	C

How to exploit charge transfer-based matrix effects in ICP-MS

1. **Introduce some carbon- sulfur- or phosphorous- containing compounds in the plasma:**

Enhance the sensitivity

Reduce spectral interferences

Compound	Analyte	Effect	Polyatomic/ isobaric Interference	Effect	Reference
n-butanol 2%	As	Signal improvement	--	--	R. Gajek, K-Y Choe, JAAS, 2015, 30, 1142-1153
CH_4	As, Se, I		ArCl, ArO, ClO, ArArH	Interferences reduced	I. Llorente, M. Gómez, C. Cámara, Spectrochim. Acta Part B, 1997, 52, 1825-1838
Ethanol 4%	As, Sb, Au		--	--	Chen, Z. Hu, S. Liu, Y. Liu, S, Gao, M. Li, K. Zong, H. Chen, S. Hu, Spectrochimica Acta Part B, 2015, 106, 36-44
	Se, Te		Kr, Xe	Interferences reduced	

How to exploit charge transfer-based matrix effects in ICP-MS

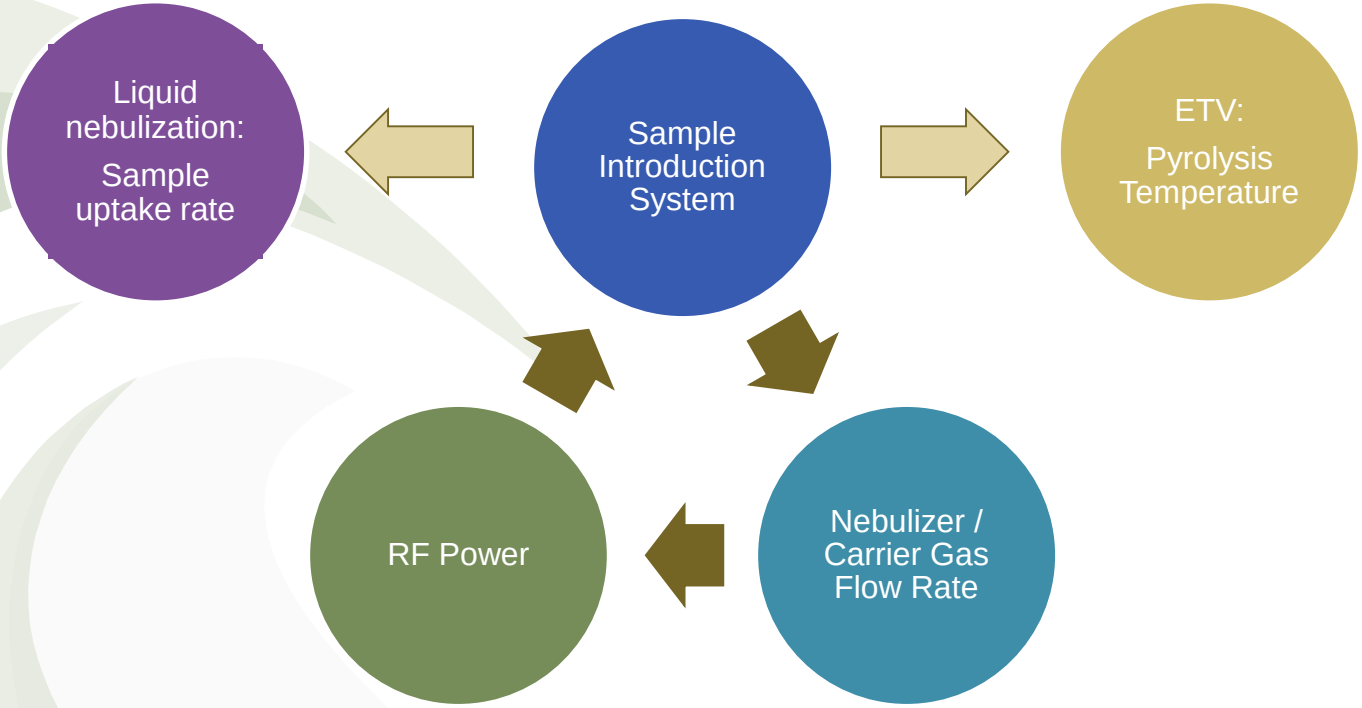
1. **Introduce some carbon- sulfur- or phosphorous- containing compounds in the plasma:**

LOD improvement

Application	Compound	Analyte	Polyatomic Interference reduced	Effect	Reference
Se in waters by ICP-MS	Lactic acid (4%) or Glycerol (4%)	Se	ArCl, Ar_2H_2, Ar_2H, Ar_2	LOD improvement	I. Llorente, M. Gómez, C. Cámara, Spectrochim. Acta Part B, 1997, 52, 1825-1838
As in drinking waters by ICP-MS	Organic solvents	As	ArCl		B. Klaue, J.D. Blum, Anal. Chem., 1999, 71, 1408-1414

How to exploit charge transfer-based matrix effects in ICP-MS

2. Optimize instrumental and experimental conditions



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A.F. Silva, B. Welz, M.T.C. de Loos-Vollebregt , Spectrochim. Acta Part B, 2008, 63, 755-762
L. Tormen, R.A. Gil, V.L.A. Frescura, L. D. Martínez, A.J. Curtius, Anal. Chim. Acta, 2012, 717, 21-27

How to exploit charge transfer-based matrix effects in ICP-MS

3. **Select the most appropriate calibration strategy**
   a. **Matrix matching**

Elemental analysis of a certified low-density polyethylene sample (ERM-EC681K) by ICP-MS after two different sample digestion procedures*

Analyte	Concentration (mg Kg^{-1})		
	Matrix HNO_3 3.3% w w^{-1}	Matrix H_2SO_4 1.4% w w^{-1} + HNO_3 2.3% w w^{-1}	Certified
As	31 ± 4	29 ± 3	29.1 ± 1.8
Cd	142 ± 5	137 ± 3	137 ± 4
Sb	111 ± 13	99 ± 5	99 ± 6
Pb	104 ± 6	94 ± 3	98 ± 6
Hg	24.9 ± 1.9	23.8 ± 1.3	23.7 ± 0.8

Acid-matched standards allows the accurate determination in a sulfuric acid matrix

*M.C. García-Poyo, G. Grindlay, L. Gras, M.T.C. de Loos-Vollebregt, J. Mora, Spectrochim. Acta Part B, 2015, 105, 71-76

How to exploit charge transfer-based matrix effects in ICP-MS

3. Select the most appropriate calibration strategy

b. Internal standarization

IS characteristics:

- Absent from the sample matrix
- Not lead to or suffer from spectral overlap
- Mass number and ionization potential close to those of the analyte
- Charge-transfer-based matrix effects similar to those suffering the analyte:
  - ✓ $^{75}As^+$ (IP = 9.79 eV) determination in biological fluids: $^{128}Te^+$ (IP = 9.01 eV)
  - ✓ $^{75}As^+$ (IP = 9.79) and $^{79}Se^+$ (9.75 eV) determination in wines: $^{197}Au^+$ (IP = 9.23)**

*M.R. Florez, E. García-Ruíz, E. Bolea-Fernández, F. Vanhaecke, M. Resano, J. Anal. At. Spectrom., 2016, 31, 245-251
** G. Grindlay, J. Mora, L. Gras, M.T.C. de Loos-Vollebregt, Anal. Chim. Acta, 2009, 652, 154-160

How to exploit charge transfer-based matrix effects in ICP-MS

Goal

Determination of ultra-trace levels of As in biological fluids by ICP-MS

Drawbacks

- Matriz composition
- Ultra-trace analyte concentration

- Unknown (depends on the sample)
- High Cl content ($^{40}Ar^{35}Cl^{+}$ on $^{75}As^{+}$)
- Organic matrices (C-effects)

External calibration with aqueous standards not useful

Sample treatment must be minimized (avoid sample contamination and analyte losses)

Strategies

- Internal standard Te (IP = 9.01)
- Sample dilution with 3% v/v Ethanol
- Matrix matching

- Minimize matrix effects (C-based)
- Reduce Cl-based interferences
- Increase As sensitivity by increasing both solution transport to the plasma and As ionization

Result

Simple and interference-free method for As determination at ultra-trace levels in biological fluids by ICP-MS

M.R. Florez, E. García-Ruíz, E. Bolea-Fernández, F. Vanhaecke, M. Resano, J. Anal. At. Spectrom., 2016, 31, 245-251

Charge transfer-based matrix effects in ICP-MS: Conclusions

- Carbon, sulfur and phosphorous-containing compounds afford charge transfer-based matrix effects in ICP-MS.
- Charge transfer-based matrix effects are magnified when increasing the amount of concomitants loading the plasma and the plasma ionization capabilities.
- Hard to ionize elements: the more the charge transfer-based matrix effects, the better its analytical response.
- Negative matrix effects are easily overcomed by using the appropriate calibration strategy.

Acknowledgements

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