

CE – Inductively Coupled Plasma – MS for the Speciation of Chromium in Leather and Skin



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Chromium



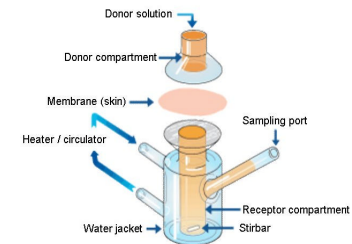
Cr(III) and Cr(VI) can induce allergic contact dermatitis

Leather contains high amounts of Cr(III) and Cr(VI), accumulated during tanning

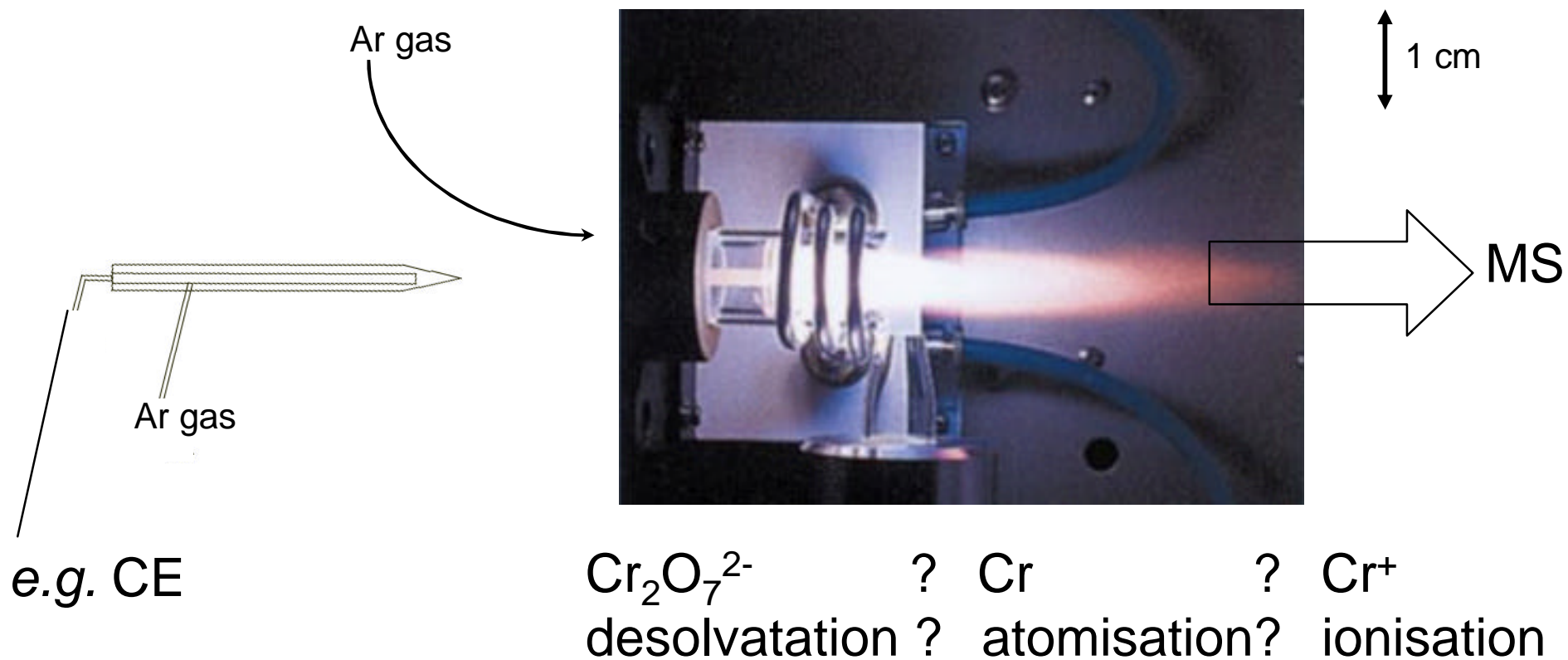


Why CE?

- Experiments with human skin
Low amount of sample
- Experiments with Franz cell
Low volumes
- Expected analytes differ in charge / mass



Inductively Coupled Plasma in CE / ICP – MS

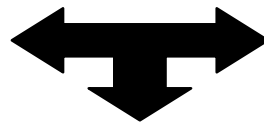
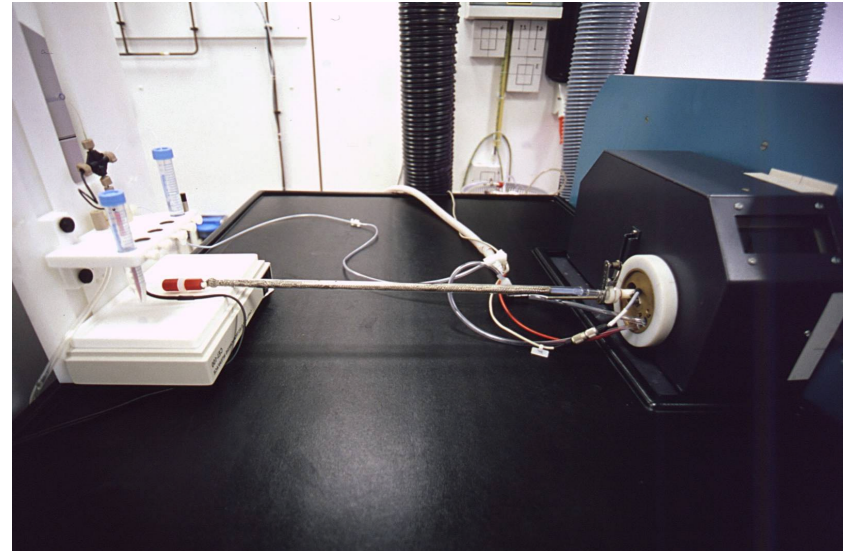


CE / ICP-MS set-up

**Agilent 3D Capillary
Electrophoresis system**

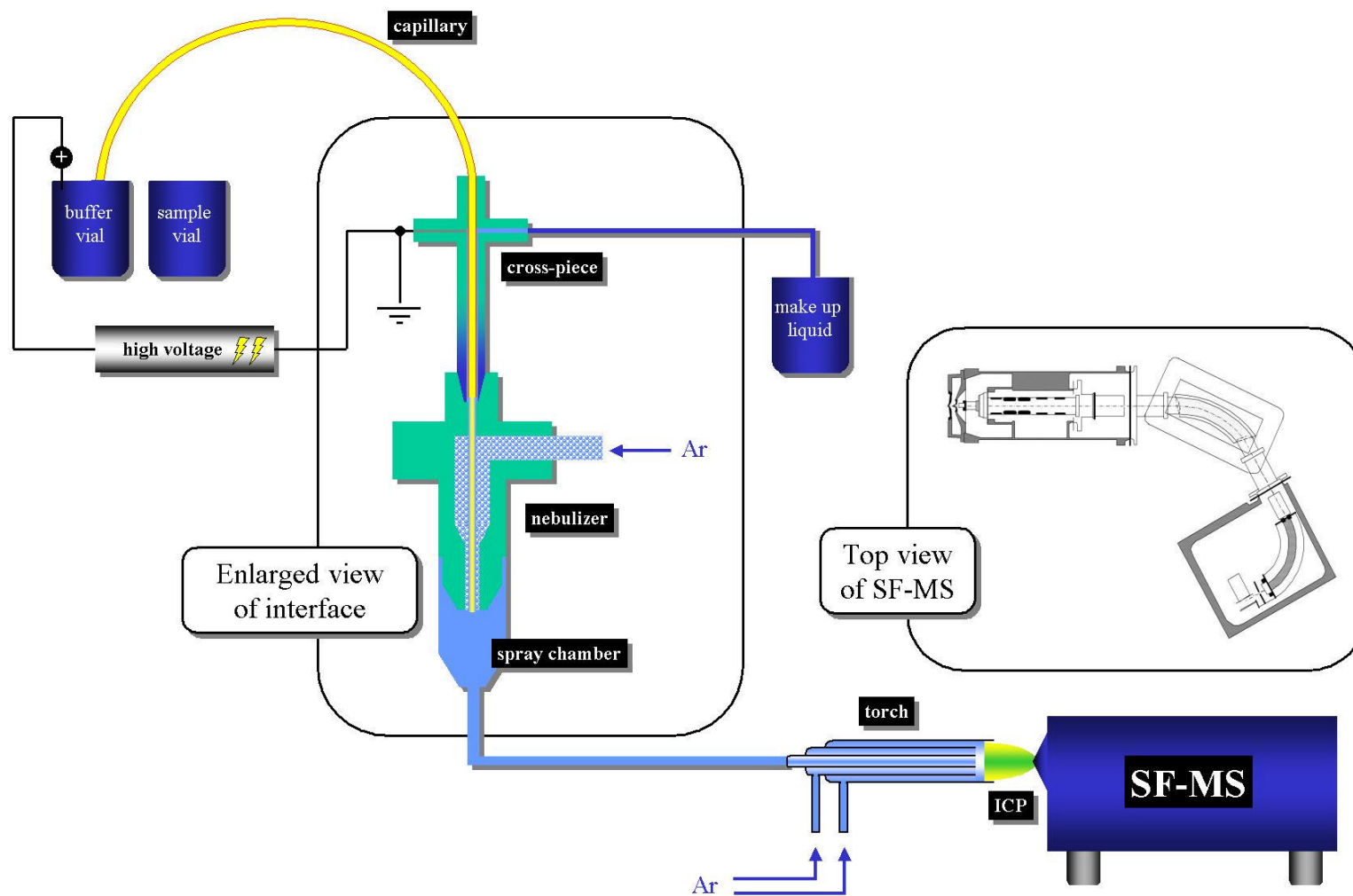


**Inductively Coupled Plasma – Sector
Field – Mass Spectrometer
(Element I, Finnigan MAT)**



**CEI-100 interface (CETAC)
Schaumlöffel, Prange**

CE / ICP-MS set-up

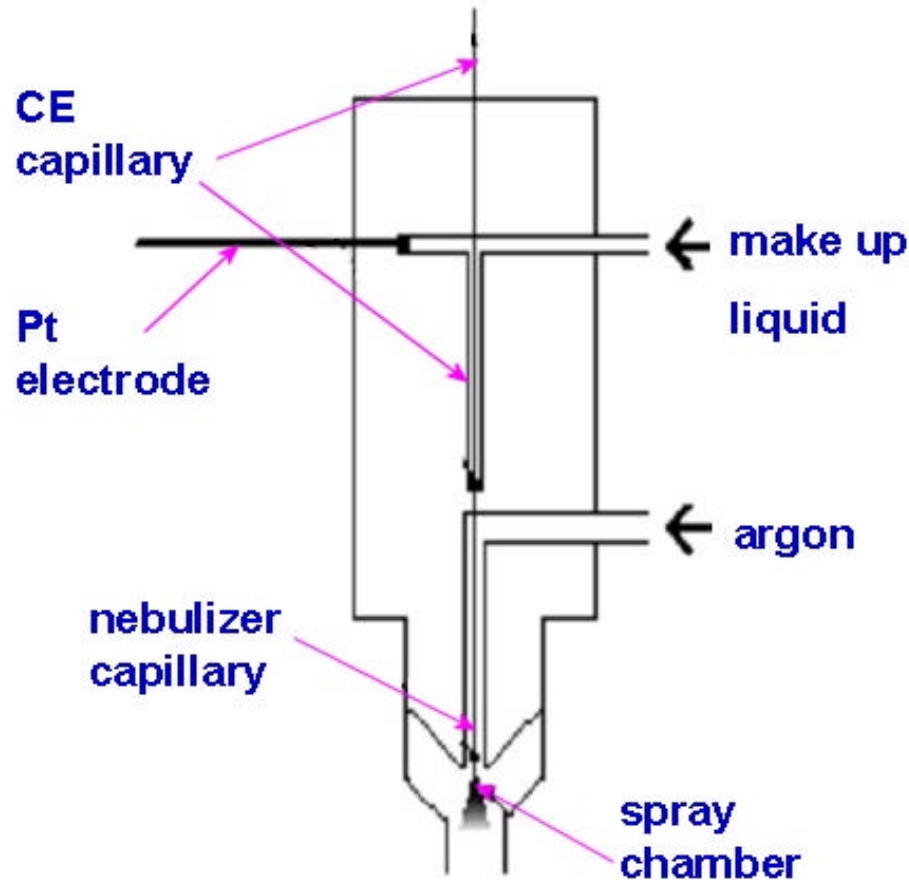


CEI-100 interface (CETAC) Schaumlöffel, Prange

No detrimental effects of suction by the nebulizer on the CE separation

Micro-concentric nebulizer

Free aspiration



Electrical connection

Adaptation of flow rates

High nebulization and analyte transport efficiency into ICP-mass spectrometer

Incubation of artificial sweat with Cr

- Chromate Cr(VI) is thought to elicit the allergy
- Yet, the vehicle leaching / transporting Cr from leather to skin is



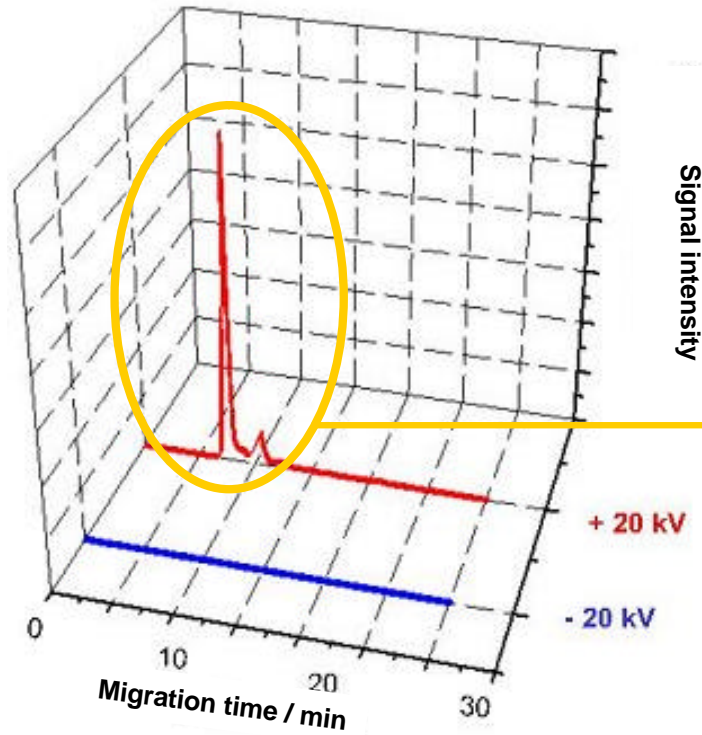
- What do Cr^{3+} and $\text{Cr}_2\text{O}_7^{2-}$ become in sweat?

Analytical set-up

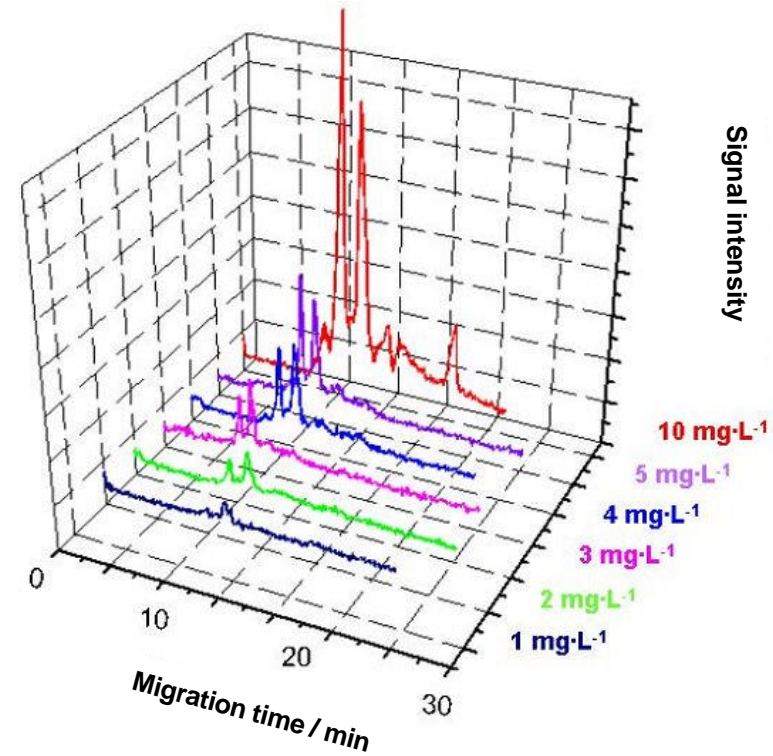
CE Voltage	+/- 20 kV No prerun derivatization!
CE Buffer	50 mmol.L ⁻¹ sodium phosphate pH 2.5 No EOF, no detection of neutral species
ICP MS Signals monitored	⁵² Cr ⁺ ⁵³ Cr ⁺

Incubation of artificial sweat with Cr³⁺

50 mg·L⁻¹ Cr(III)



1-10 mg·L⁻¹ Cr(III)



- 20 kV → no peaks → no anions → no oxidation products

+ 20 kV → Cr(III) complexes

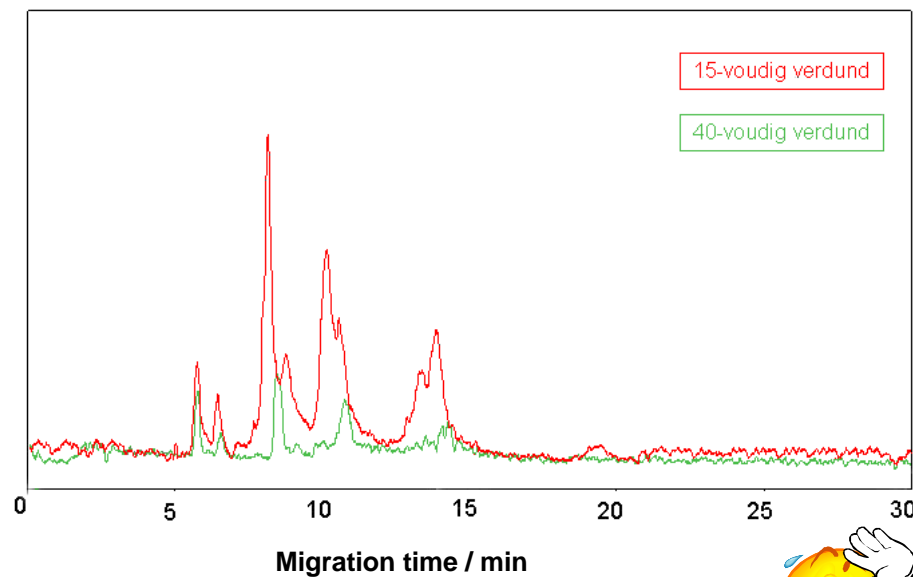
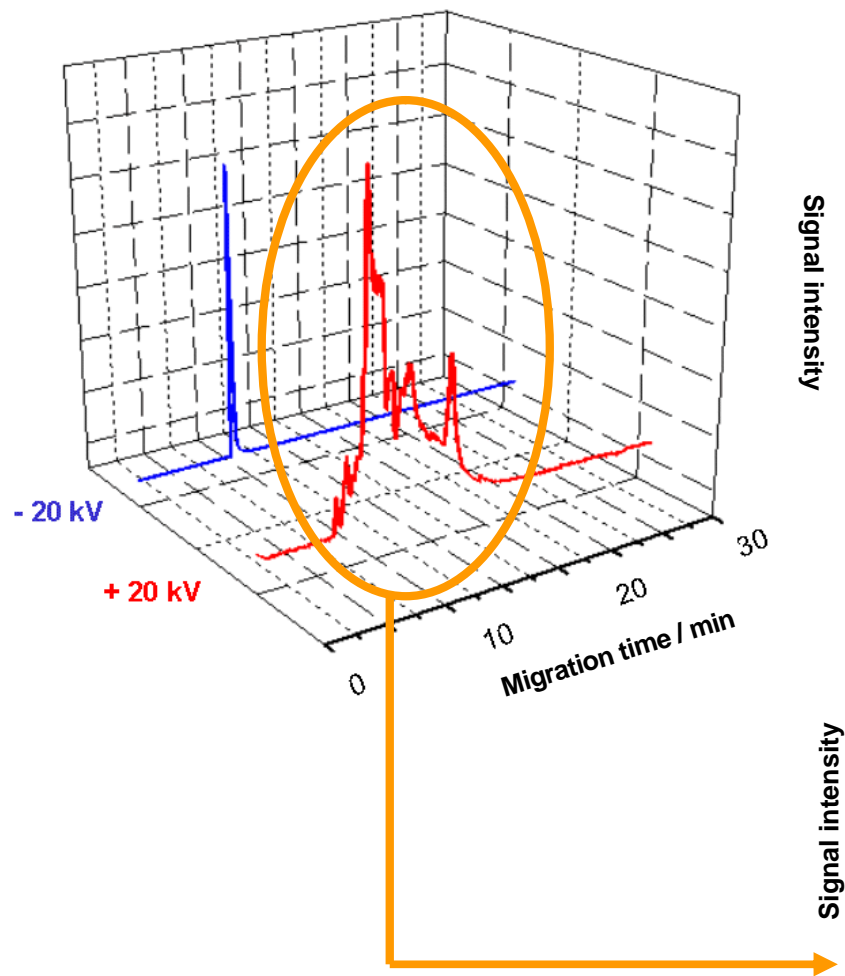


Incubation of artificial sweat with Cr(VI)

500 mg·L⁻¹ Cr(VI) in sweat

- 20 kV → one peak → (di)chromate

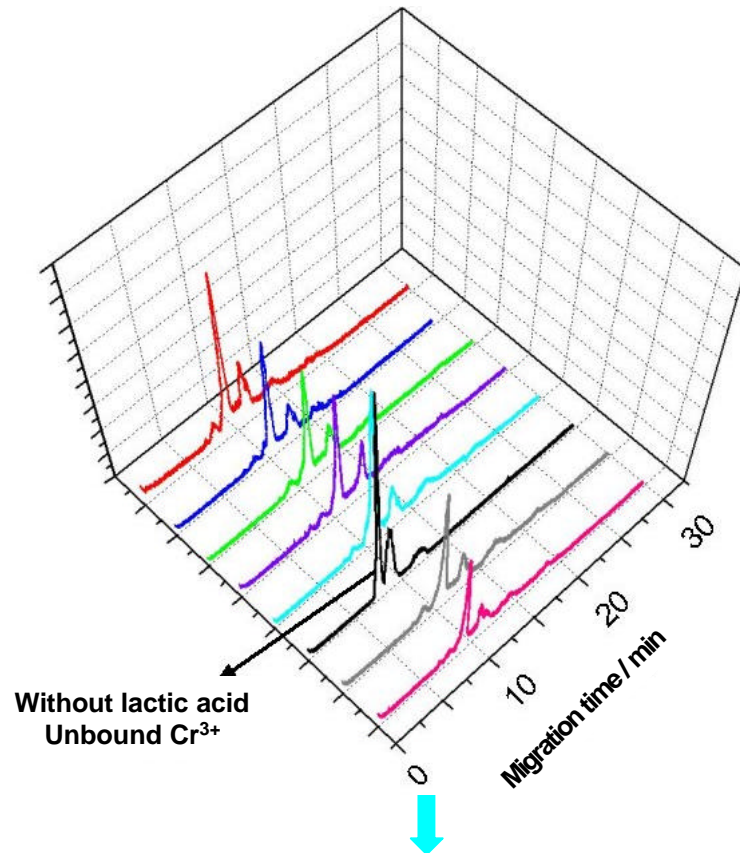
+ 20 kV → positively charged complexes → Cr(III) complexes



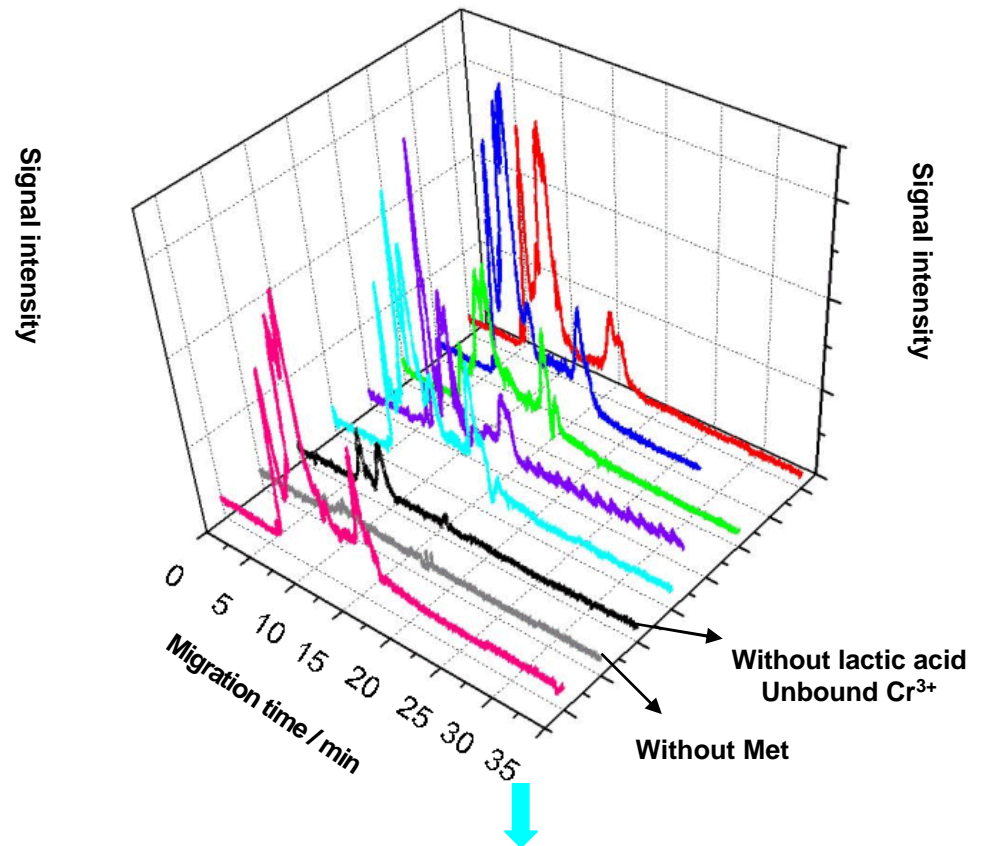
Cr in sweat

Characterization of the Cr-species

Cr(III) added, +20 kV



Cr(VI), added, +20 kV



Methionine = reduction of Cr(VI)





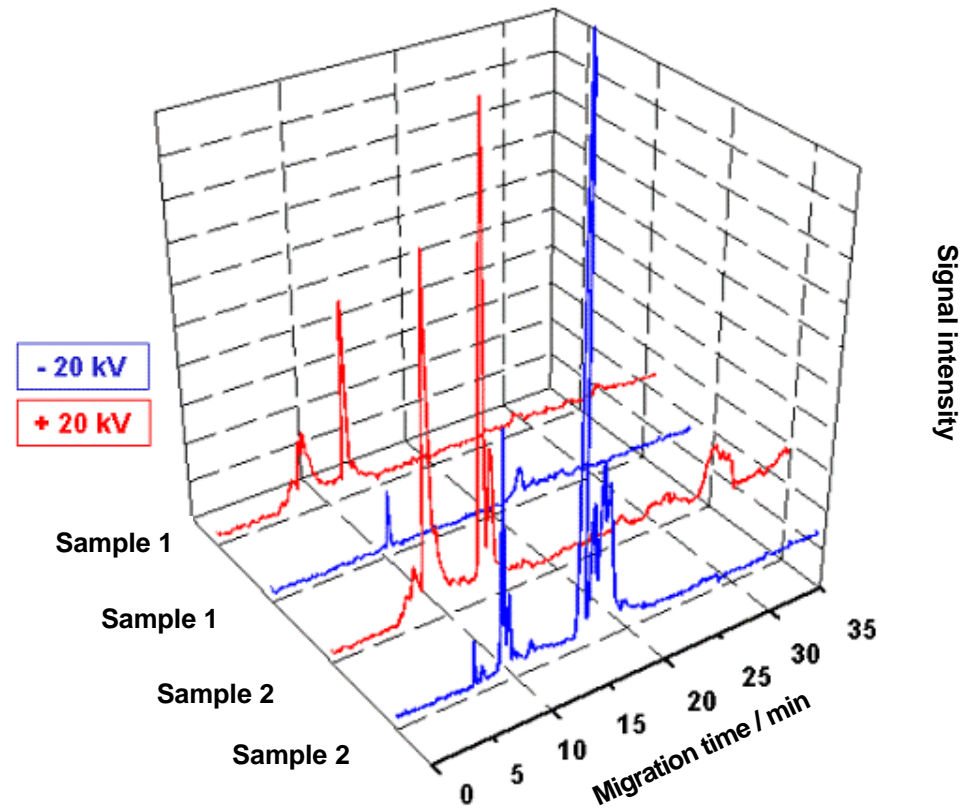
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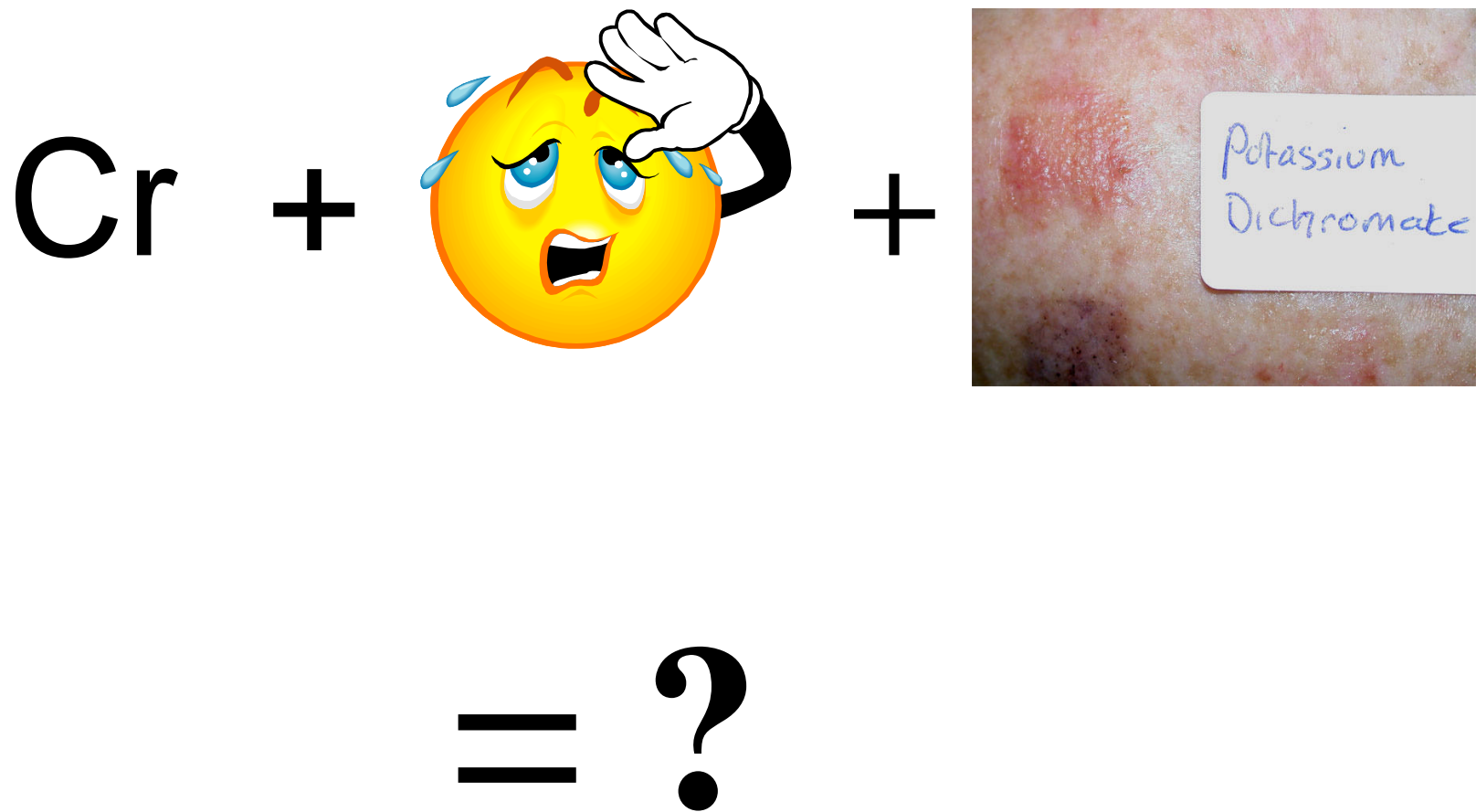
Leaching from leather



Cr after leaching of leather with sweat

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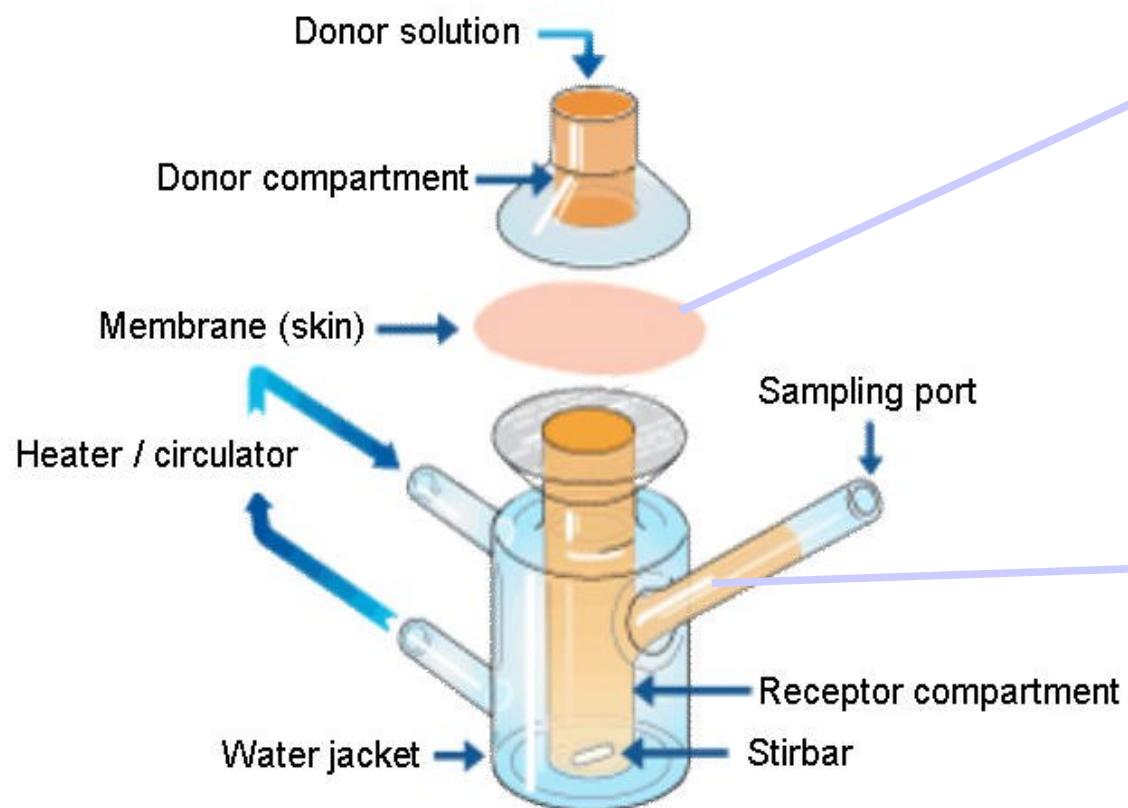
Cr in sweat alone



Anal Bioanal Chem 2006, 384, 378–384

In vitro permeation of chromium through skin

Diffusion cell



Analysis of:

Porcine or human skin

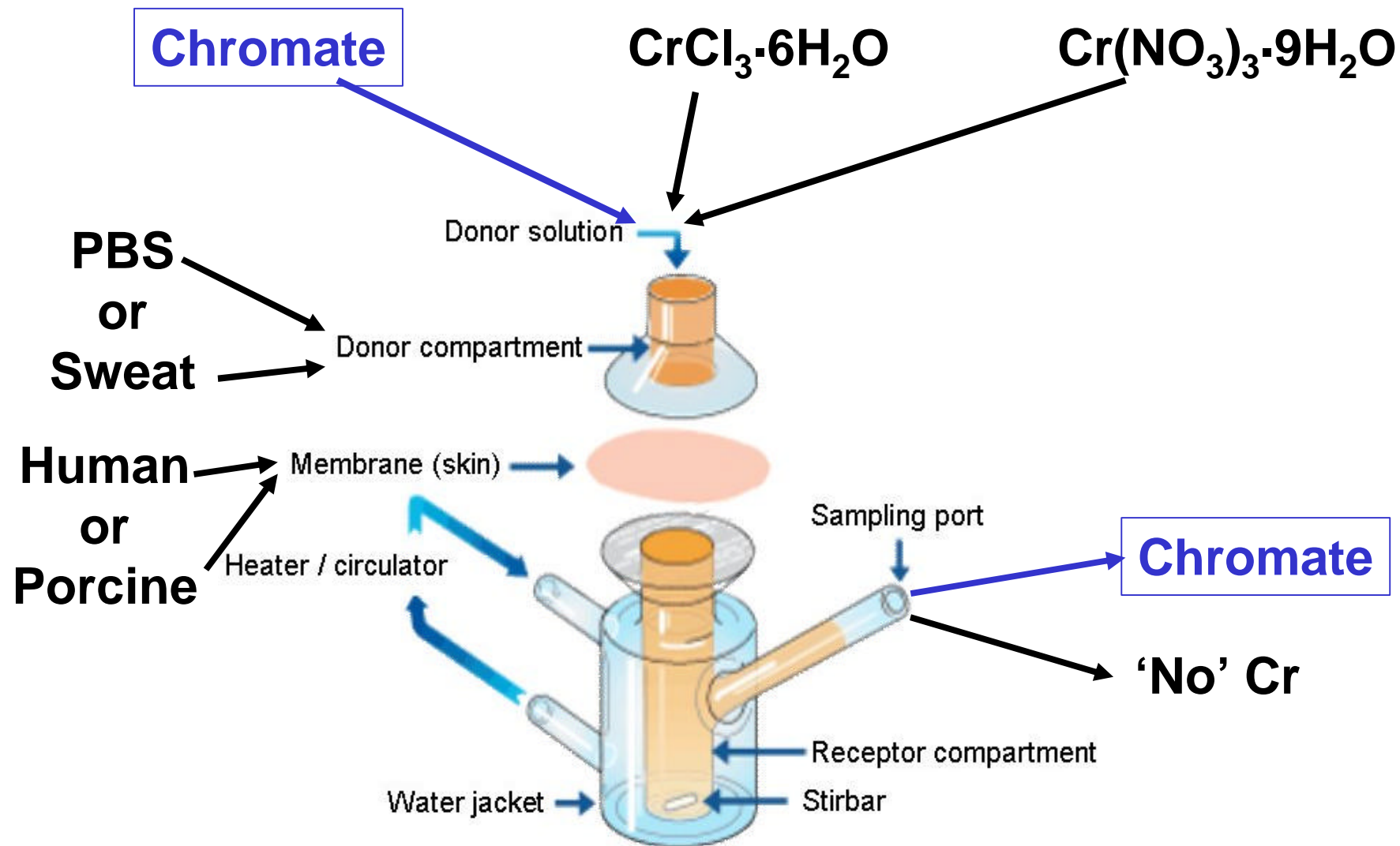


Microwave-assisted acid digestion-PN-ICP-SF-MS

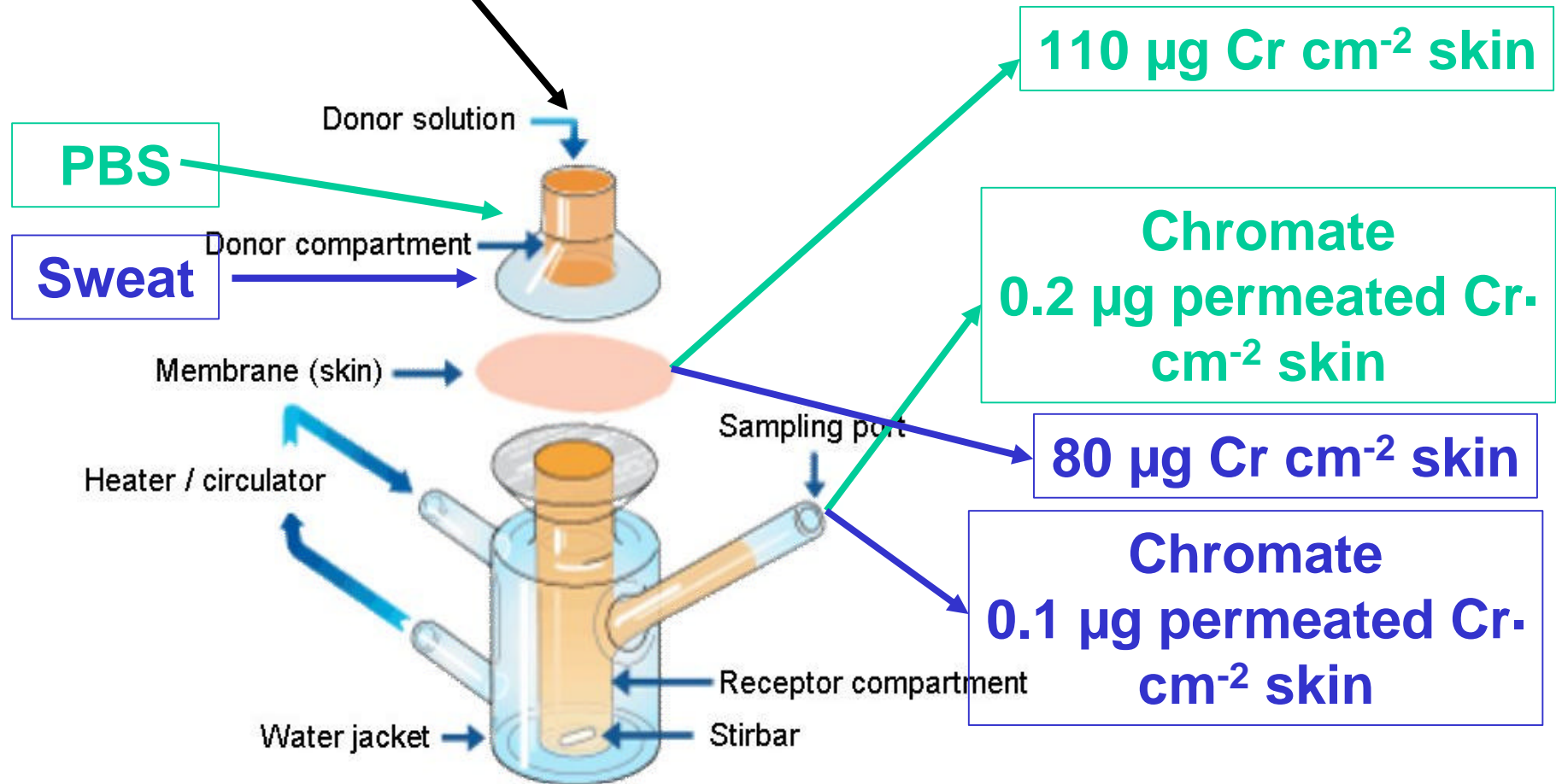
Receptor fluid (PBS)



CE-ICP-SF-MS



Chromate
0.034 mol Cr·L⁻¹



Conclusions

Analytics:

- Hyphenation between CE and ICP-MS ideal for studies of metals in biomolecules, even in complex matrices.

Cr allergy:

- Synergetic effect between leather / Cr / sweat
- Chromate diffuse
- Still much to do!



The end!

Questions?

Concentration $K_2Cr_2O_7$ (%)	μg permeated $\text{Cr}\cdot\text{cm}^{-2}$ <i>porcine</i> skin		μg permeated $\text{Cr}\cdot\text{cm}^{-2}$ <i>human</i> skin
Aqueous solutions	Only chromate detected		
0.25	< LOD		< LOD
0.5	0.18	0.17	0.18
1.0	0.19	0.21	0.20
2.5	0.21	0.23	0.23
5.0	0.24	0.25	0.25
Incubated in simulated sweat	Only chromate detected		
0.25	< LOD		< LOD
0.5	0.12	0.13	0.10
1.0	0.15	0.15	0.12
2.5	0.16	0.17	0.15
5.0	0.17	0.20	0.16