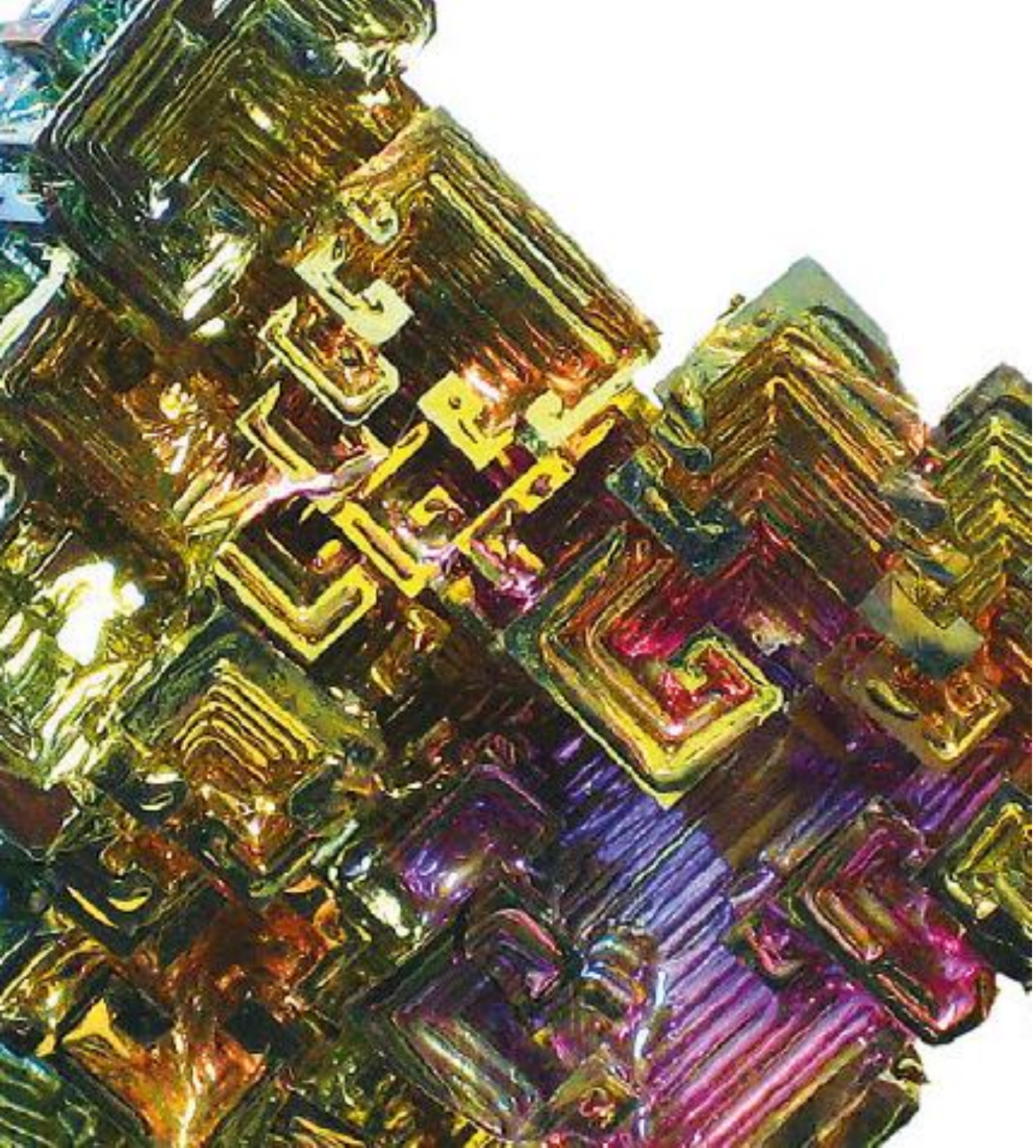


A New Generation of Sensors for Mercury-Free Analysis of Heavy Metals

Kia Williams, PhD

August 3, 2023

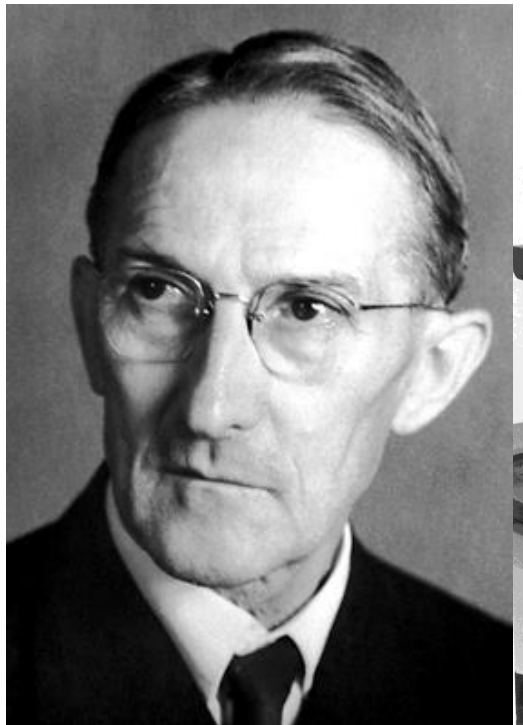
Voltammetry

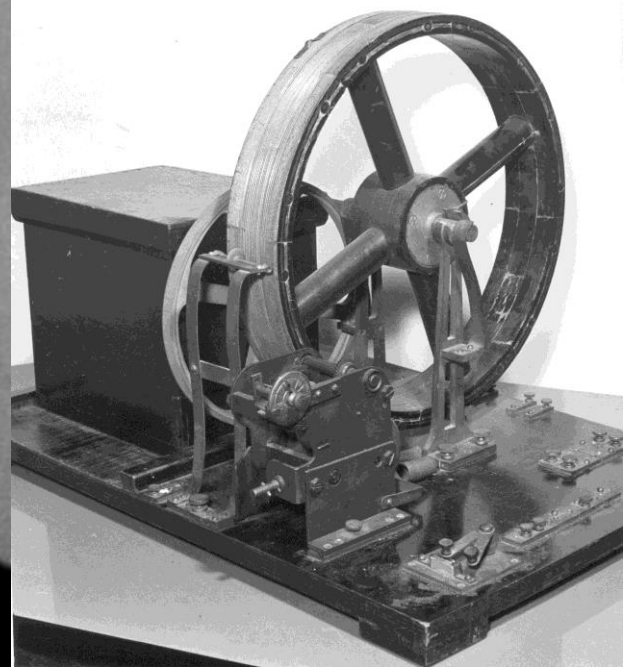
Voltammetry = Volt-Am(pero)-Metry

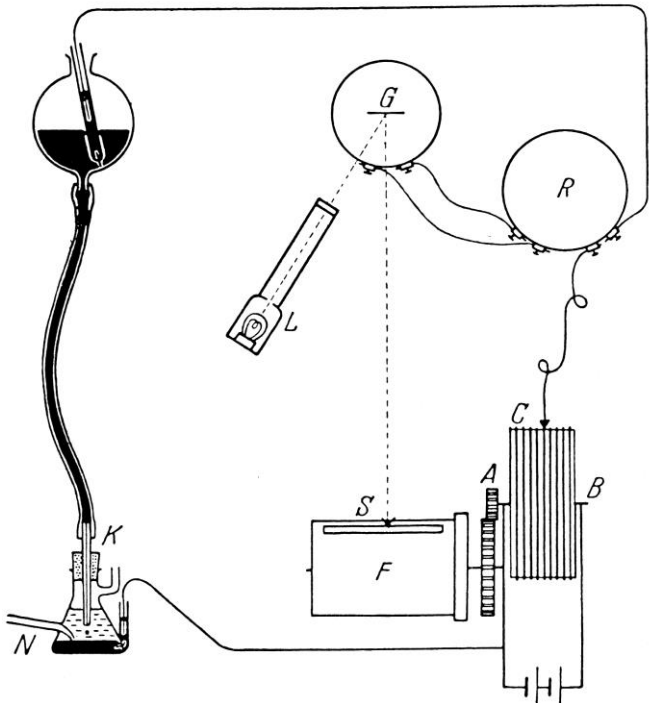
- Voltage ramp applied to electrode
- Current measured

Method first described 1922 by Heyrovsky

Nobel Prize 1959







Voltammetry

- Information about the analyte in the electrochemical cell is obtained by measuring the current as the potential is varied with time, I = f(U)

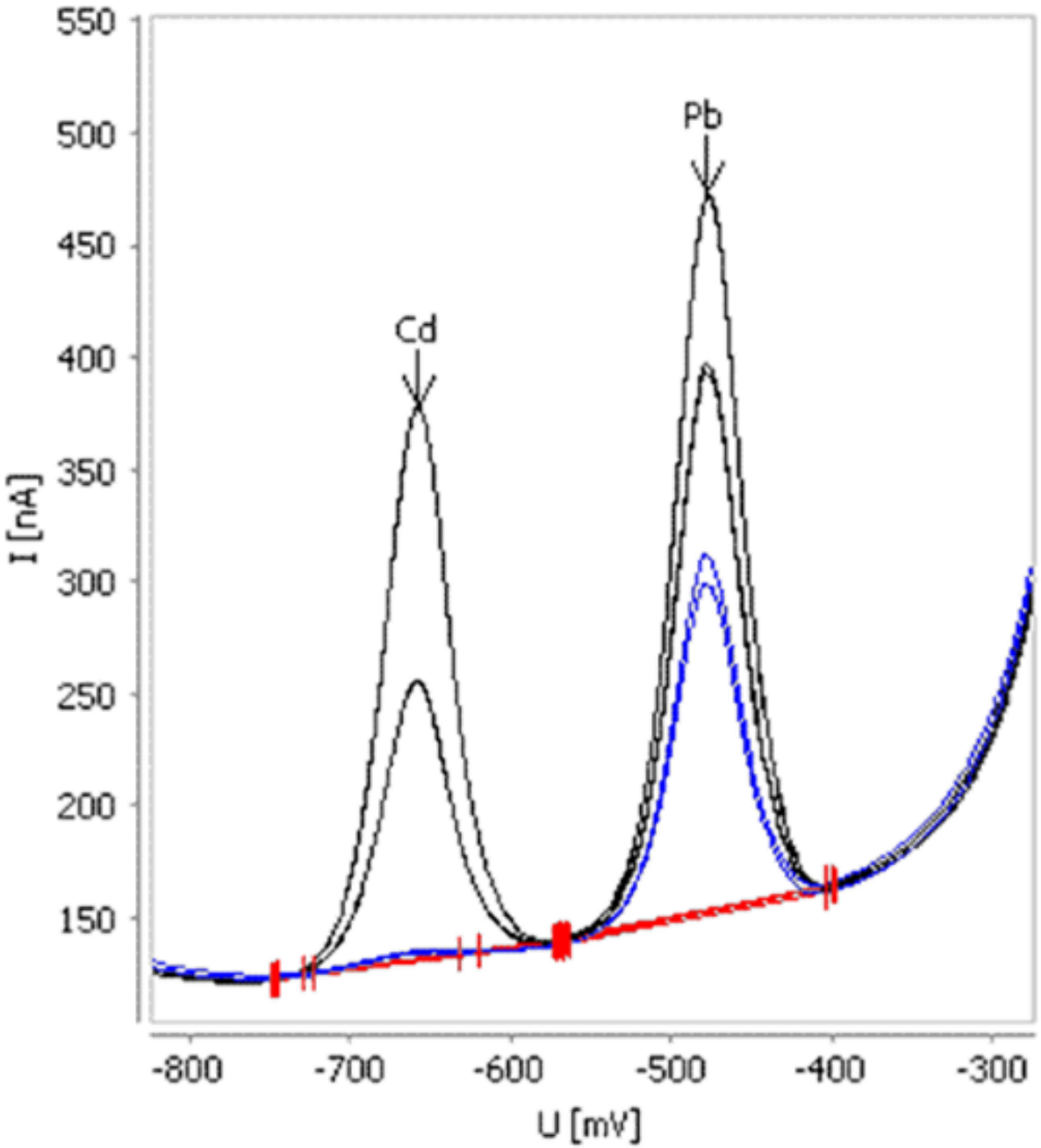
- Mercury has been the standard electrode material since the invention of polarography

A typical voltammetric application

Determination of Cd and Pb in tap water

Results:

- Cadmium 0.02 µg/L
- Lead 1.77 µg/L

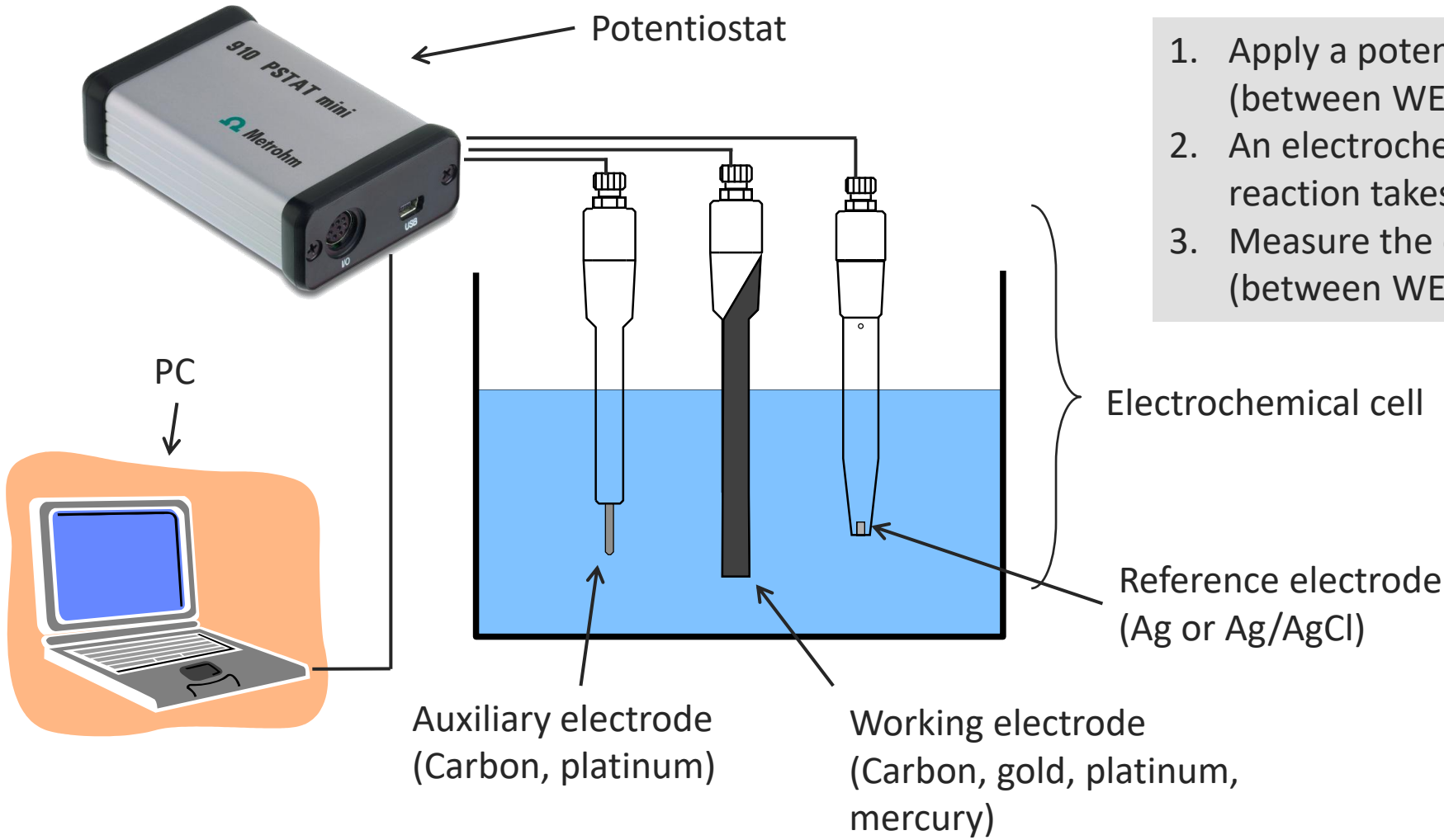


Comparison of Voltammetry with competitive techniques

	FAAS	GFAAS	ICP-OES	XRF	ICP-MS	VA
LOD	1 ppm	> 50 ppt	1 ppb	1 ppm	sub-ppt	ppb/ppt
Linear range	3-4	2-3	4-6	3-4	Up to 9	1-3
Interferences						
• Chemical	Many	Many	Some	None	Some	Many
• Spectral	Some	Many	Some	Some	Some	Very few
• Matrix	Many	Many	Some	Some	Few	Many
Speed						
No. elements						
• Typical no.	50	35	55	35	70	30-35
Multi-element	No	No	Yes	Yes	Yes	No (max 4)
• Simultan.	No	No	Yes	Yes	Yes	No (max 4)
Sample size	mL	µL	mL	>10 g	µL or mL	mL
Capital cost	$	$$	$$	$$	$$$	$
Operating cost	$	$$	$$$	$$	$$$	$

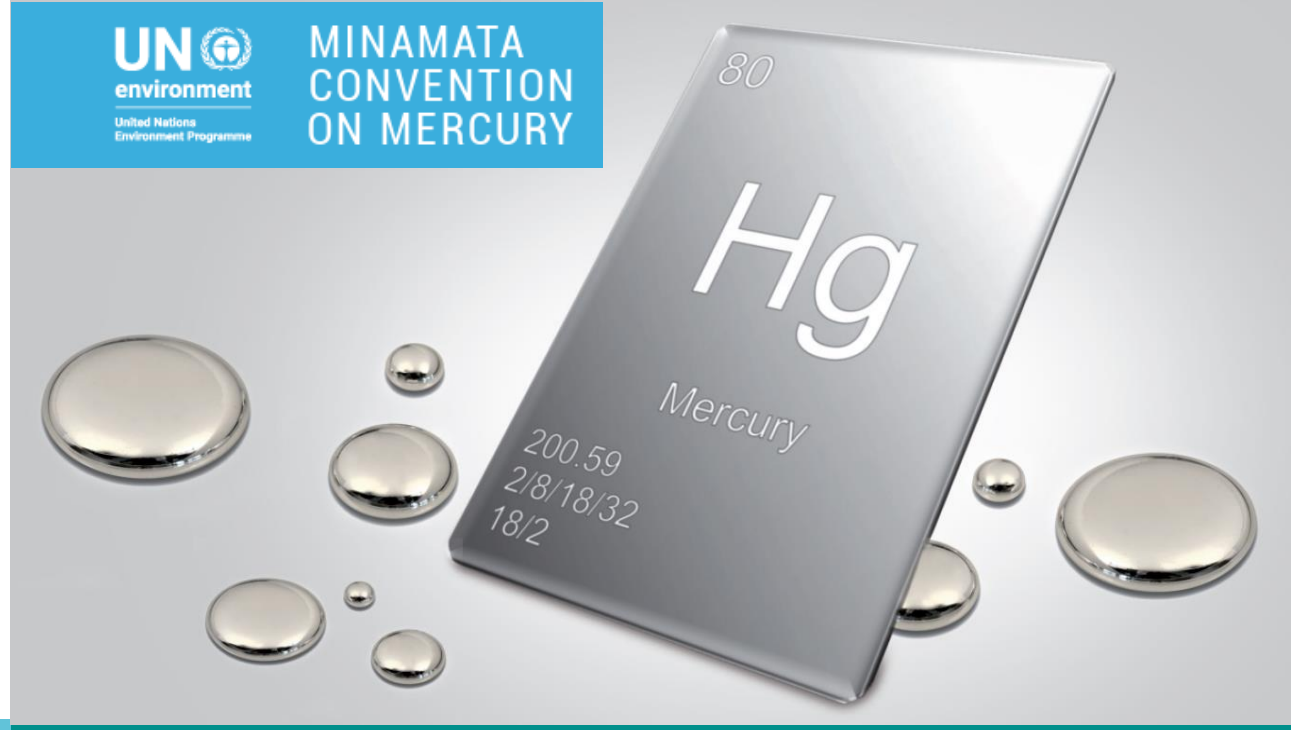
Source: Agilent eSeminar: ICPMS - A replacement for USP 231

Instrumentation



1. Apply a potential (between WE and RE)
2. An electrochemical reaction takes place
3. Measure the current (between WE and AE)

Why do we need new electrodes?



Minamata Convention on Mercury

- Regulations to reduce the use and release of mercury
- Includes trade restrictions
- Entry into force: August 2017
- Signed by 128 countries, ratified by 102 countries

Future regulations

- More trade restrictions are possible
- Permissions and inventories may be required for customers

Working range of different electrode materials

Oxidation of electrode

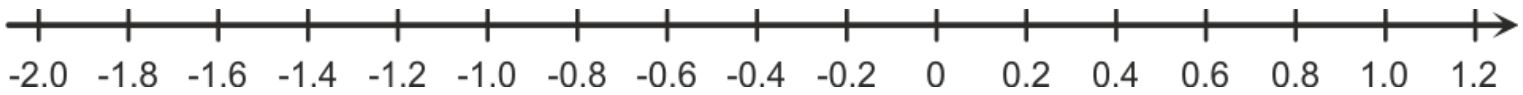
Mercury

Carbon (Glassy Carbon, Ultra Trace)

Gold

Platinum

Potential (V)



Reduction of electrolyte
e.g. $H^+ + e^- \longrightarrow H$

Mercury vs. Solid-state electrodes

Advantages of mercury

- Versatility (metals, organics, anions)
- Each drop is a new electrode (ideal surface)
- No electrochemical pretreatment
- Large potential range
- Highest possible linear range

Advantages of solid-state electrodes

- Simple mechanical handling
- Not toxic
- Good acceptance
- Price (Screen-printed electrodes)

Disadvantages of mercury

- Toxic material
- Acceptance problem
- Regulatory obstacles
- Logistics problems (purchase, waste)
- Maintenance requires know-how

Disadvantages of solid-state electrodes

- Quality of electrode surface critical
- Electrode performance changes over time
- Electrode preparation required (mechanical, electrochemical)
- Linearity, matrix interferences, lifetime

Alternatives -new developments in Metrohm

- scTRACE Gold
  - Electrode designed for determination of As (and Hg)
- Bi drop electrode
- Screen-printed electrodes (SPE) for voltammetry

Solid-state electrodes applications

Goals for method development

Electrodes, methods

- Mercury-free methods
- Mercury film acceptable if no viable alternative available

Sample matrix

- Organic-free drinking water
- Water with high hardness (approx. 500 mg/L Ca)
- Water with high salinity (artificial sea water with approx. 35 g/L NaCl)
- Other sample matrices if relevant application field identified

Sensitivity

- Limit of detection <=10% of WHO limit value for drinking water (if existing)
- National lower limit values taken into consideration if possible

Linearity

- Min. 10% … 100% of limit value or better

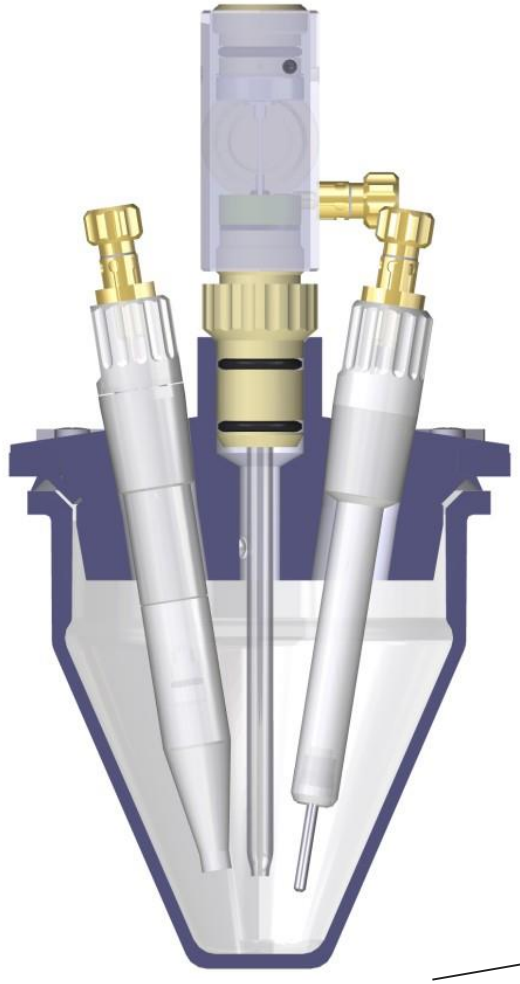
Combined sensor

1 sensor combining:

- Working electrode
- Auxiliary electrode
- Reference electrode

Examples

- scTRACE Gold
- SPE (screen-printed electrode)



Screen-printed electrode

scTRACE Gold

Applications with the scTRACE Gold

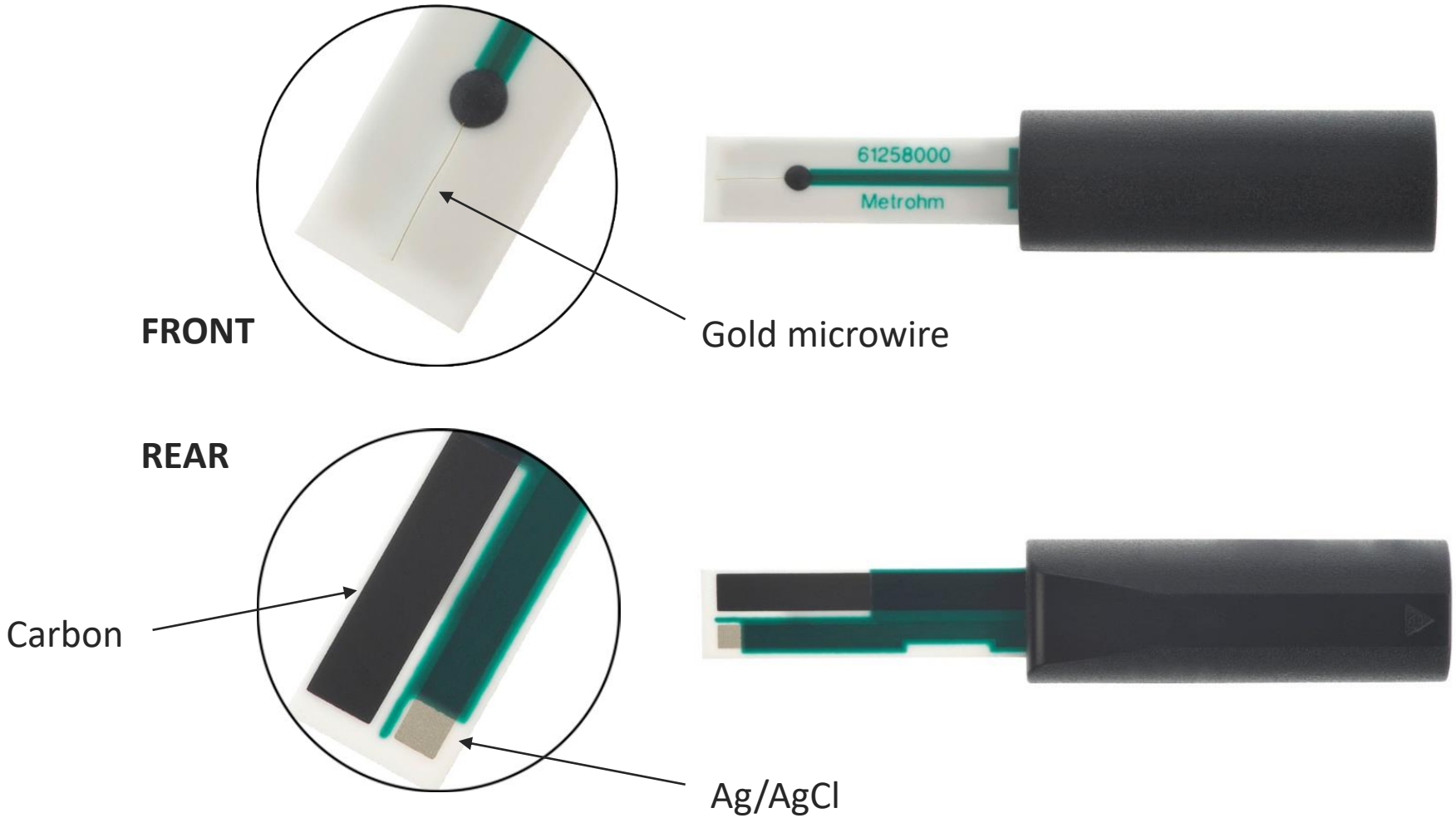
scTRACE Gold

Front

- Working electrode: Gold microwire

Rear

- AE: Carbon
- RE: Ag/AgCl



Pb in drinking water

Electrode

- scTRACE Gold (with Ag film)

Electrolyte

- c(citric acid) = 0.045 mol/L
- c(KCl) = 0.009 mol/L
- c(NaOH) = 0.009 mol/L

Conditions

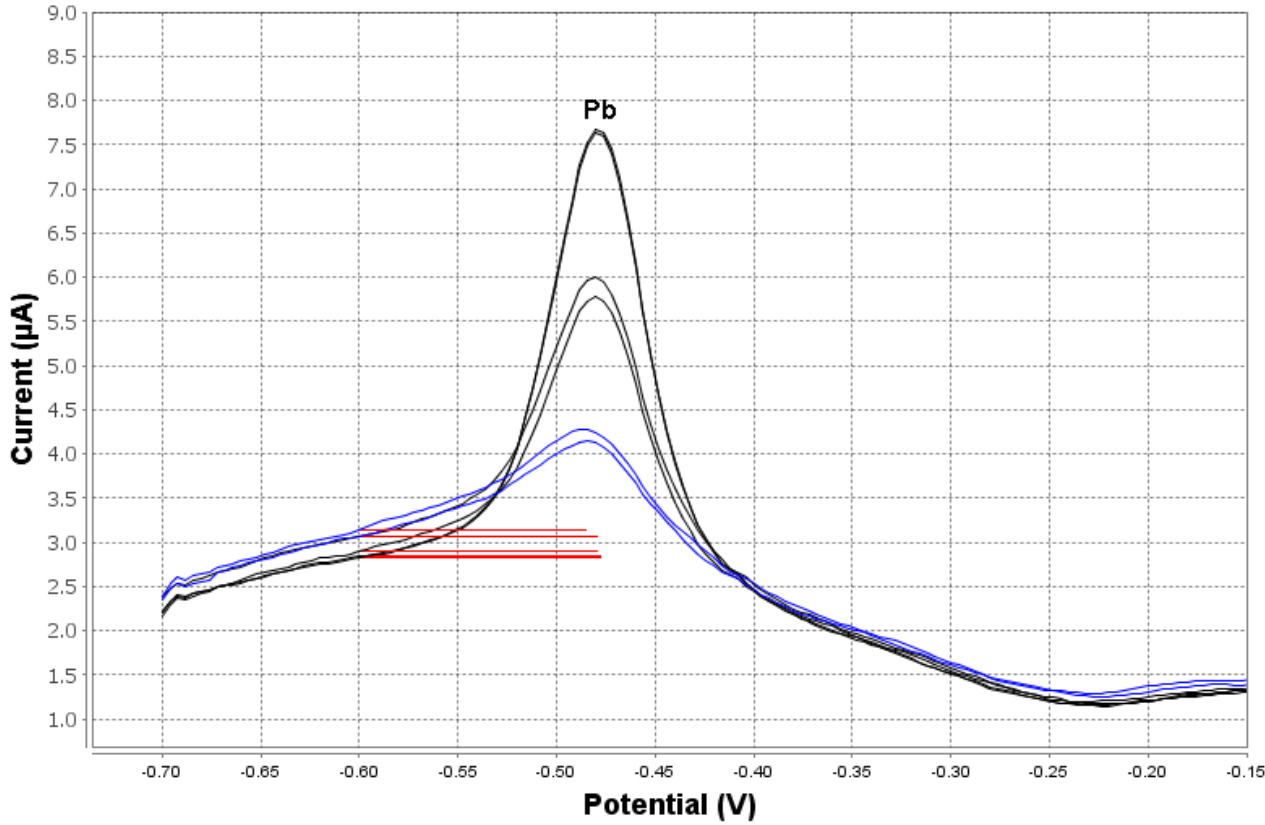
- Deposition: -0.7 V, 30 s
- Sweep: -0.7 V … -0.3 V

Sample size

- 15 mL

Result

- β(Pb) = 2.8 µg/L



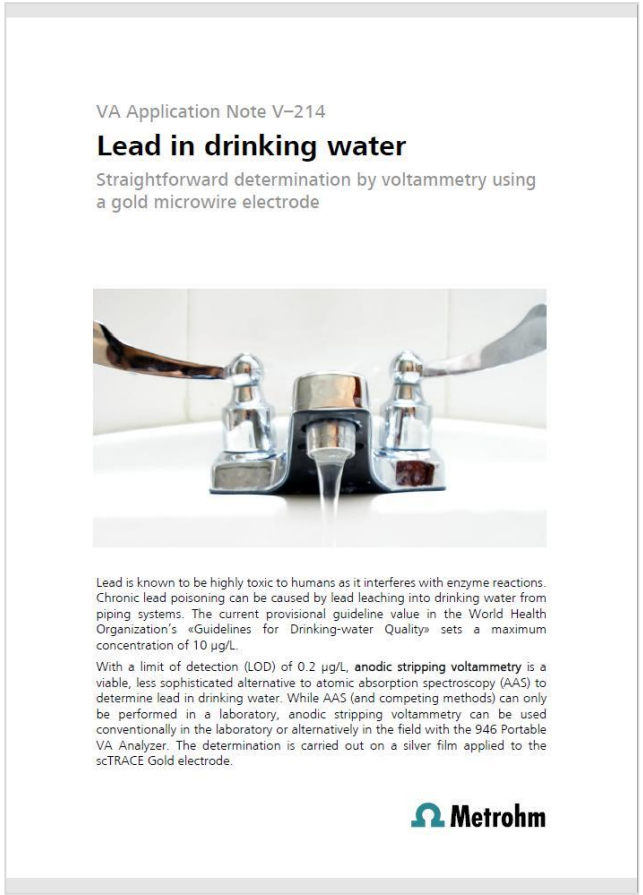
Lead in water with the scTRACE Gold (Ag film)

Limit of detection, linear range

Deposition time	Limit of detection	Linear range
30 s	0.4 µg/L	25 µg/L
60 s	0.2 µg/L	15 µg/L

Important to know

- Ex-situ Ag film. No Ag addition to the sample
- Remove Ag film at the end of the day («Cleaning» method)


VA Application Note V–214

Lead in drinking water

Straightforward determination by voltammetry using a gold microwire electrode

Lead is known to be highly toxic to humans as it interferes with enzyme reactions. Chronic lead poisoning can be caused by lead leaching into drinking water from piping systems. The current provisional guideline value in the World Health Organization's «Guidelines for Drinking-water Quality» sets a maximum concentration of 10 µg/L.

With a limit of detection (LOD) of 0.2 µg/L, **anodic stripping voltammetry** is a viable, less sophisticated alternative to atomic absorption spectroscopy (AAS) to determine lead in drinking water. While AAS (and competing methods) can only be performed in a laboratory, anodic stripping voltammetry can be used conventionally in the laboratory or alternatively in the field with the 946 Portable VA Analyzer. The determination is carried out on a silver film applied to the scTRACE Gold electrode.

Metrohm

Application Bulletin 433
Application Note V-214

Detection limits in water according to WHO guidelines

Analyte	Limit value*	Limit of detection**
Antimony	20 µg/L	1 µg/L
Arsenic	10 µg/L	1 µg/L
Bismuth	-	1 µg/L
Cadmium	3 µg/L	0.3 µg/L
Chromium	50 µg/L	2 µg/L
Cobalt	-	1 µg/L
Copper	2000 µg/L	0.5 µg/L
Iron	-	10 µg/L
Lead	10 µg/L	0.2 µg/L
Mercury	6 µg/L	0.5 µg/L
Nickel	70 µg/L	1 µg/L
Selenium	10 µg/L	2 µg/L
Tellurium	-	1.5 µg/L
Thallium	-	10 µg/L
Zinc	-	5 µg/L

*As specified in the Guidelines for Drinking-water Quality of the World Health Organization

**Limits of detection when used with the 946 Portable VA Analyzer

Electroless Ni baths

Bismuth determination

Electrode
- scTRACE Gold

Electrolyte
- c(HCl) = 0.1 mol/L

Conditions
- Deposition: -0.1 V, 30 s
- Sweep: -0.2 V … +0.3 V

Sample size
- 0.02 mL

Result
- β(Bi) = 0.45 mg/L

Pb determination

Electrode
- scTRACE Gold (with Ag film)

Electrolyte
- c(citric acid) = 0.045 mol/L
- c(KCl) = 0.009 mol/L
- c(NaOH) = 0.009 mol/L

Conditions
- Deposition: -0.7 V, 30 s
- Sweep: -0.7 V … -0.3 V

Sample size
- 0.05 mL

Result
- β(Pb) = 0.9 mg/L

Applications with carbon screen-printed electrodes

Screen-printed electrode

SPE

AE: same as WE, or carbon, ...

WE: carbon, gold, platinum, etc.

RE: silver, or silver chloride, ...

Ni, Co in drinking water

Electrode

- Carbon SPE (Metrohm Dropsens 11L, ex situ Bi film)

Electrolyte

- Ammonia buffer, DMG, bismuth solution

Conditions

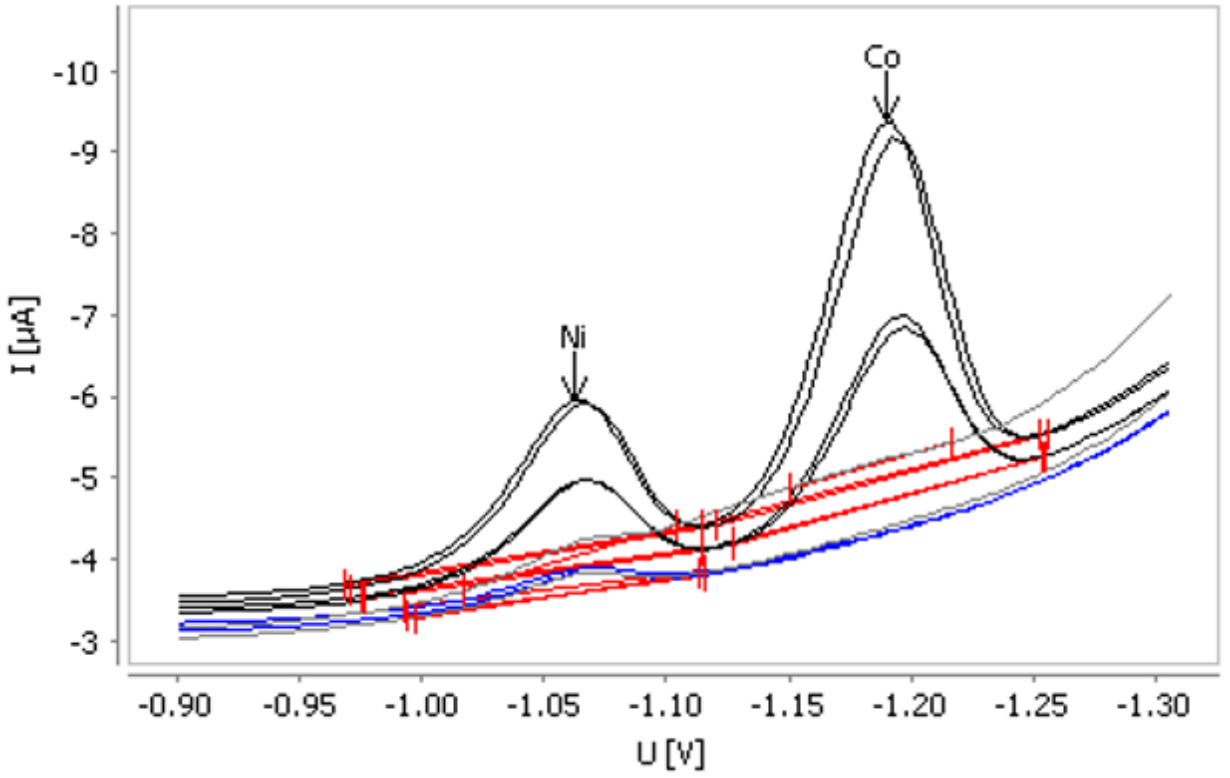
- Deposition: -0.9 V, 30 s
- Sweep: -0.9 V … -1.3 V

Sample Size

- 10 ml or 15 ml

Result

- B(Ni) = 0.56 µg/L
- B(Co) = -



Ni, Co in water (carbon SPE, ex situ Bi film)

Limit of detection, linear range

Deposition time	Limit of detection	Linear range
30 s (946*)	1 µg/L	10 µg/L
30 s (884**)	0.4 µg/L	10 µg/L

Important to know

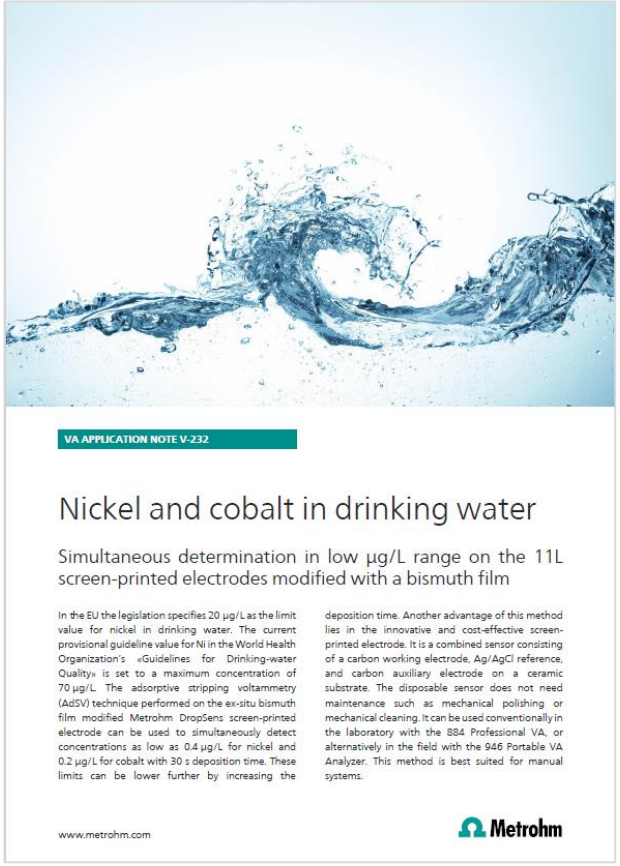
Ex situ Bi film. No Bi addition to sample.

Plating solution can be used 10 times

Bi film lasts for 3–5 measurements

Removal of Bi film not necessary

*946 Portable VA
**884 Professional VA



Application Note V-232

Applications with the Bismuth drop electrode

Bismuth drop electrode

Description

- Novel type of electrode
- Bismuth drop made of molten bismuth metal
- Glass body

Applications

- Cd, Pb in water samples
- Ni, Co in water samples
- Fe in water samples

Cd and Pb in ground water

Electrode

- Bi drop electrode

Electrolyte

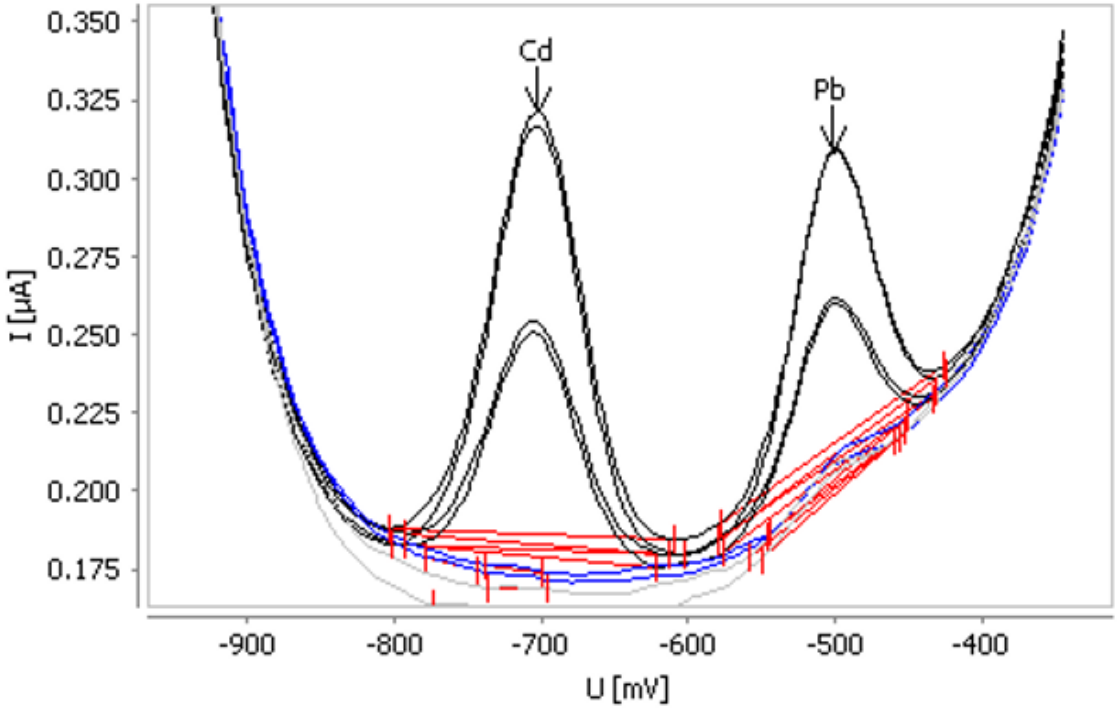
- c(acetic acid) = 2 mol/L
- $c(NH_3)$ = 1 mol/L)

Conditions

- Differential pulse
- Deposition: -1.1 V (60 s)
- Sweep: -1 V … -0.35V

Result

- β(Cd) = < LOD
- β(Pb) = < LOD



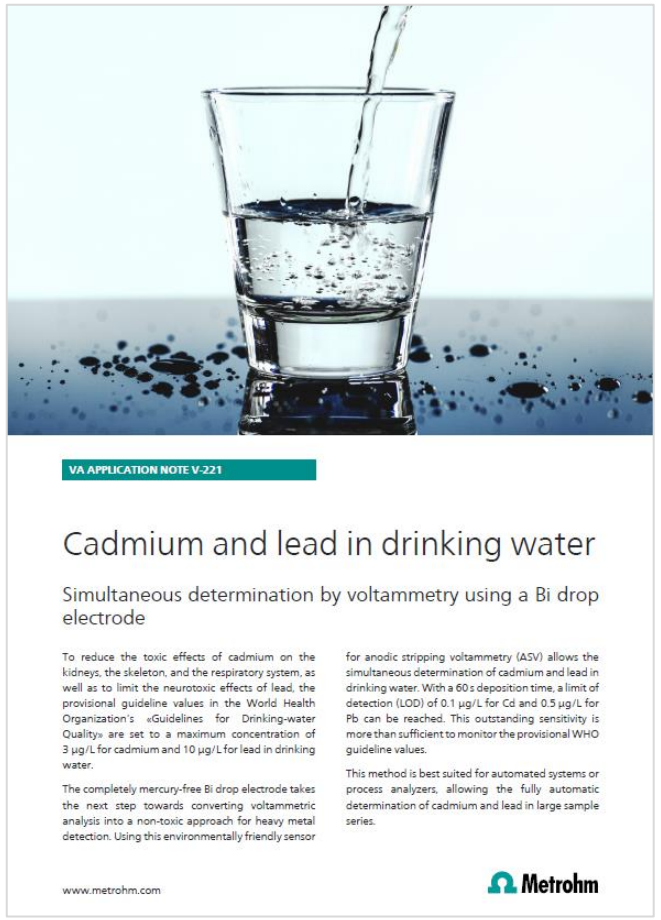
Cadmium, lead at the Bi drop electrode

Limit of detection, linear range

Deposition time	Limit of detection	Linear range
Cd (30 s)	0.1 µg/L	15 µg/L
Pb (30 s)	0.5 µg/L	15 µg/L

Important to know

- Hg free method
- Activation of the Bi drop required



Application Bulletin 438/1
Application Note AN V- 221

Cd and Pb determination

RECOVERY

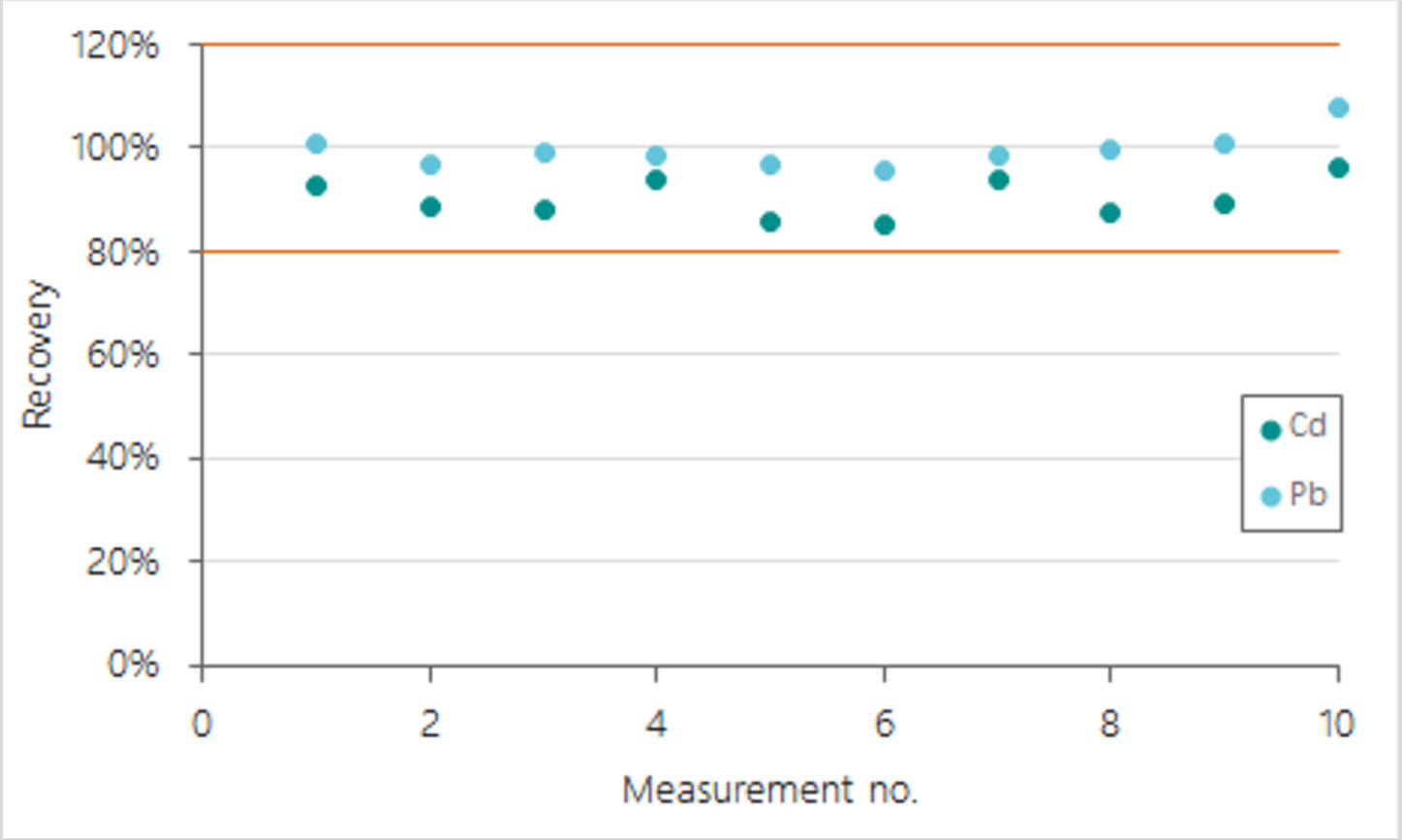
β(Cd) = 1 µg/L: 90.2%

β(Pb) = 5 µg/L: 99.5%

REPEATABILITY (RSD)

Cd: ± 4%

Pb: ± 3%



Application documents for Bi drop electrode

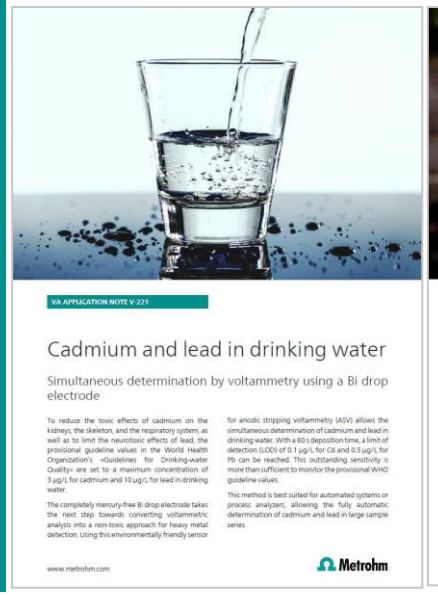
APPLICATION BULLETINS

- 438 – Cd, Pb
- 439 - Fe
- 440 – Ni, Co

APPLICATION NOTES

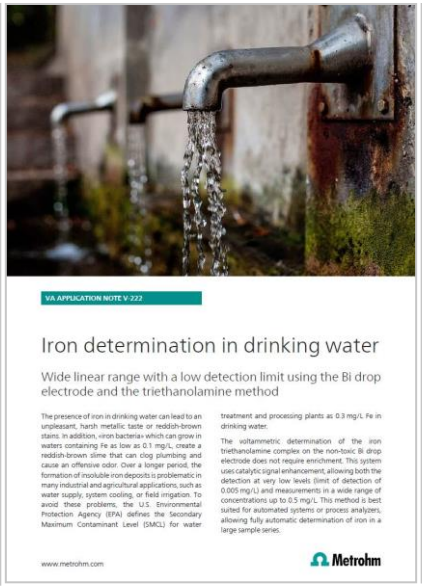
- V-221 – Cd, Pb
- V-222 – Fe
- V-223 – Ni, Co

Element	LOD [µg/L]	Linear range [µg/L]
Cd	0.1	0.1–15
Pb	0.5	0.5–15
Ni	0.2	0.2–8
Co	0.1	0.1–12
Fe	5	5–500


VA APPLICATION NOTE V-221

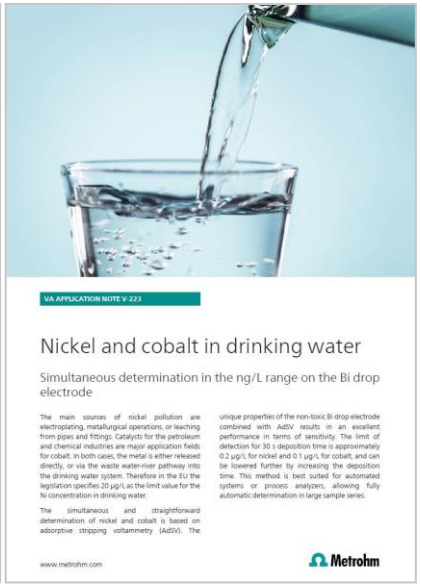
Cadmium and lead in drinking water

Simultaneous determination by voltammetry using a Bi drop electrode


VA APPLICATION NOTE V-222

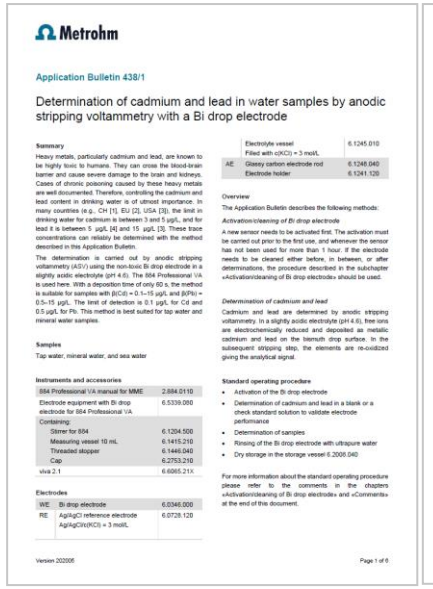
Iron determination in drinking water

Wide linear range with a low detection limit using the Bi drop electrode and the triethanolamine method

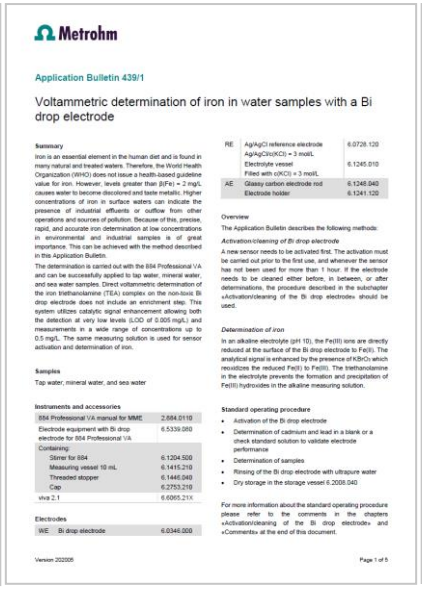

VA APPLICATION NOTE V-223

Nickel and cobalt in drinking water

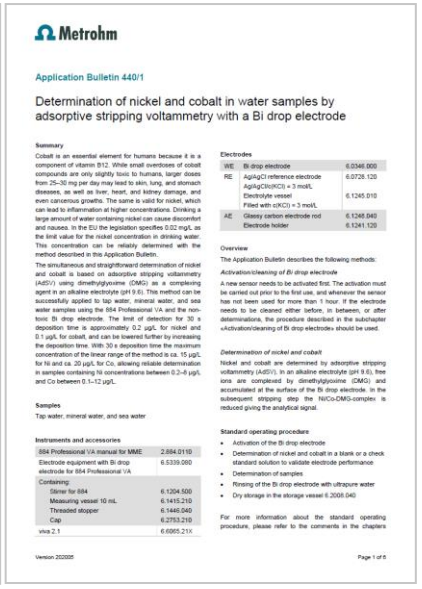
Simultaneous determination in the ng/L range on the Bi drop electrode


Application Bulletin 438/1

Determination of cadmium and lead in water samples by anodic stripping voltammetry with a Bi drop electrode


Application Bulletin 439/1

Voltammetric determination of iron in water samples with a Bi drop electrode


Application Bulletin 440/1

Determination of nickel and cobalt in water samples by adsorptive stripping voltammetry with a Bi drop electrode

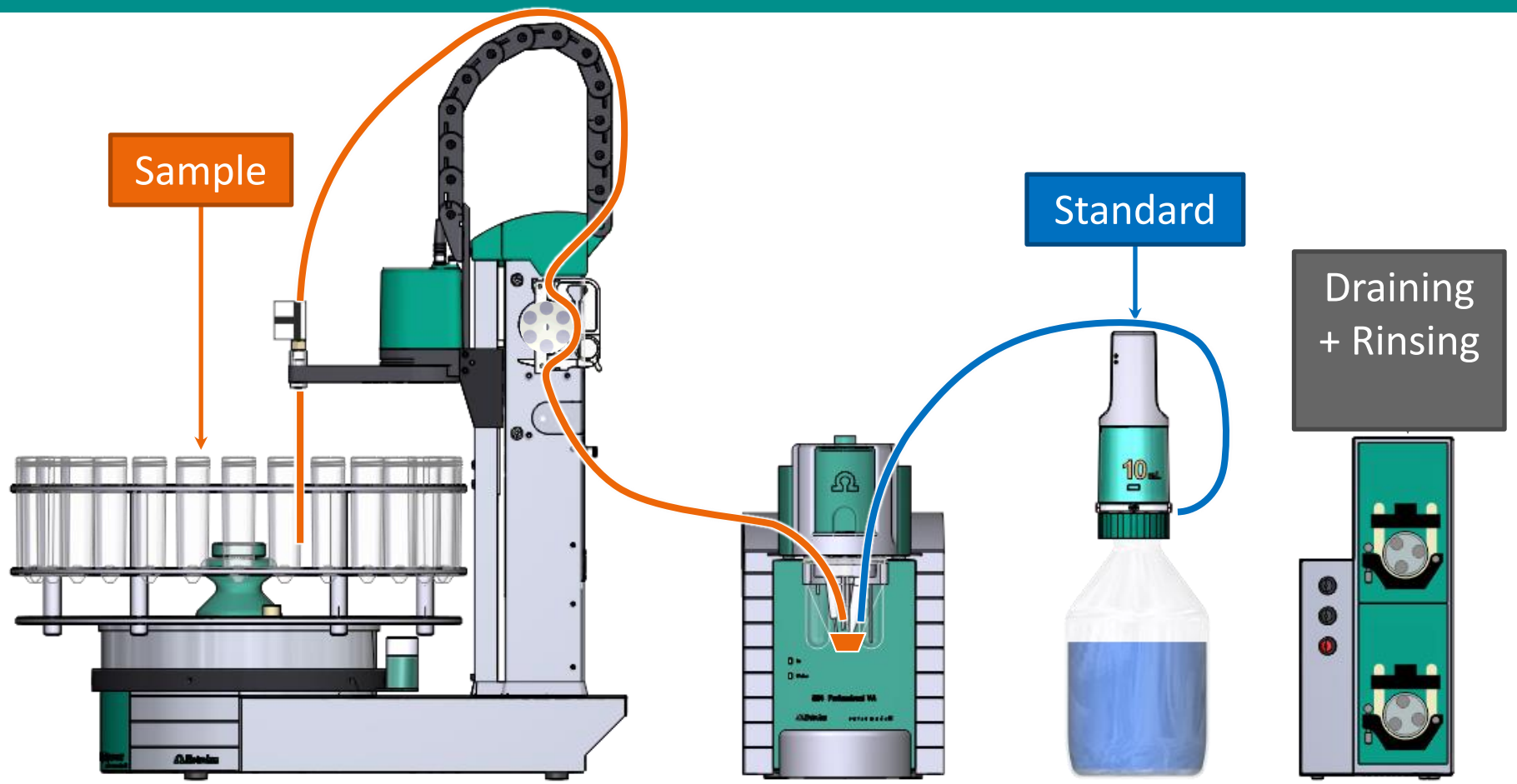
Implementation

Field Measurements

946 Portable VA

- On-site determination
- Battery powered
- Predefined methods
- Solid state electrodes-SPEs and scTrace Gold

Manual or Automated Liquid Handling



884 Professional VA

- Manual or automated
- High throughput

- Solid-state electrodes
  - scTrace Gold
  - Carbon SPE
  - Bi drop electrode
  - Rotating disk electrode (RDE)

Online Measurements

ADI2045VA Process Analyzer

- Online control of water and wastewater quality and industrial mining processes
- Can be equipped with a UV or thermal digester module
- Solid-state electrodes
  - scTrace Gold
  - Rotating disk electrode (RDE)

QUESTIONS?

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