

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

Kia Williams, PhD

August 3, 2023

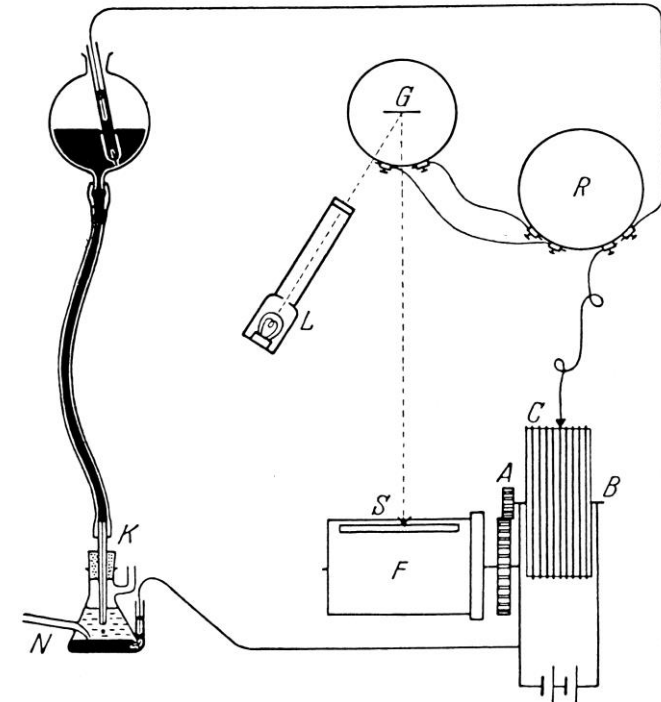
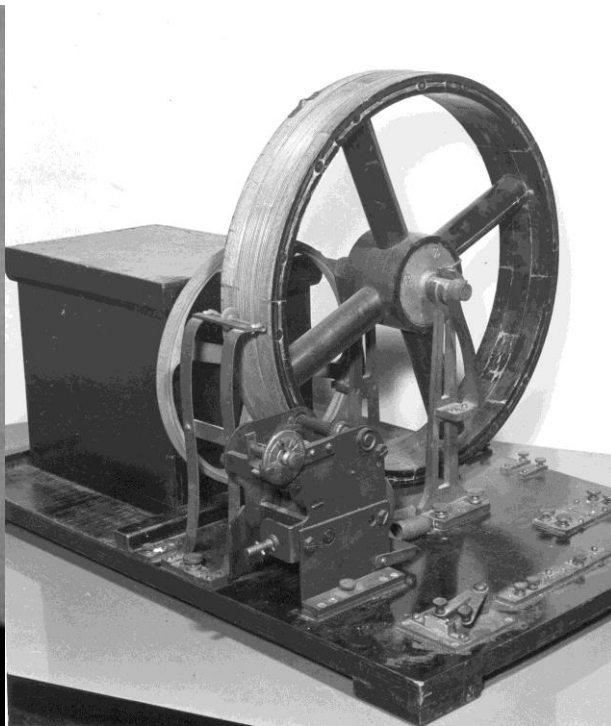
Voltammetry

Voltammetry = Volt-Am(pero)-Metry

- Voltage ramp applied to electrode
- Current measured

Method first described 1922 by Heyrovsky

Nobel Prize 1959



Voltammetry

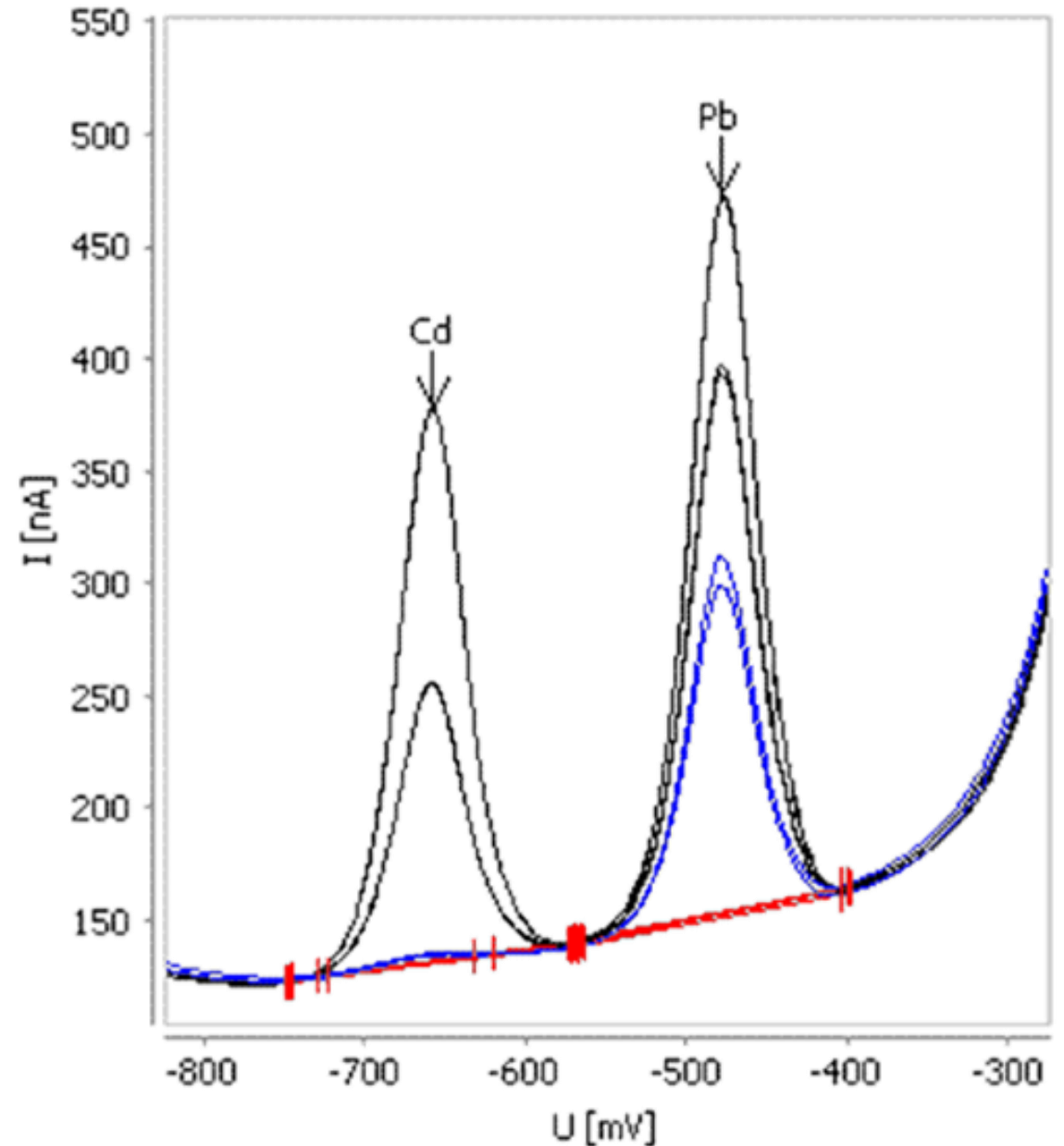
- Information about the analyte in the electrochemical cell is obtained by measuring the current as the potential is varied with time, $I = f(U)$
- Mercury has been the standard electrode material since the invention of polarography

A typical voltammetric application













Determination of Cd and Pb in tap water

Results:

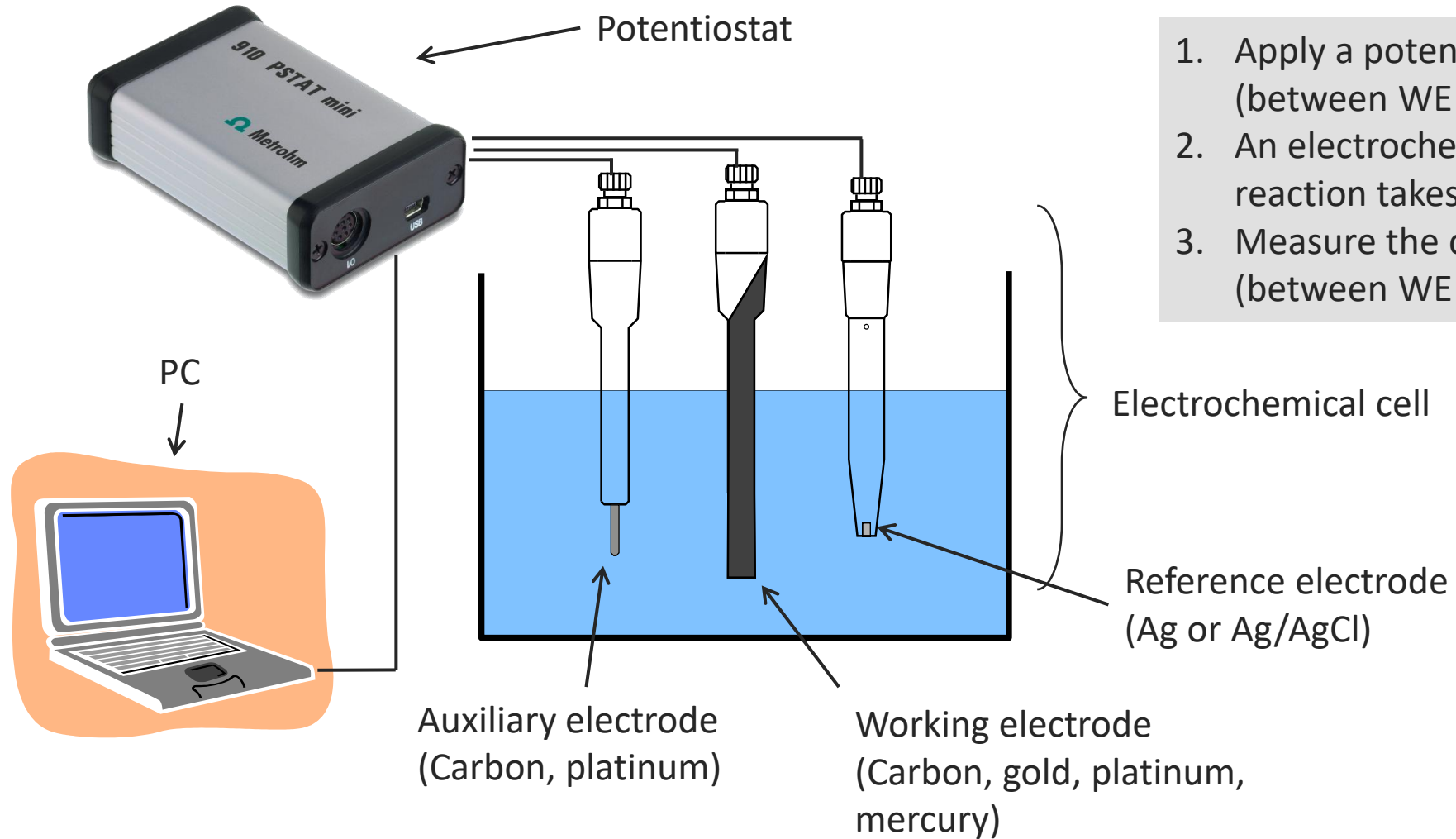
- Cadmium 0.02 $\mu\text{g/L}$
- Lead 1.77 $\mu\text{g/L}$



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	\$	\$\$	\$\$\$	\$\$	\$\$\$	\$

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)



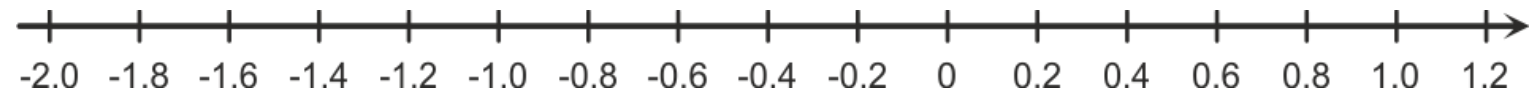
Gold



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 $\leq 10\%$ 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

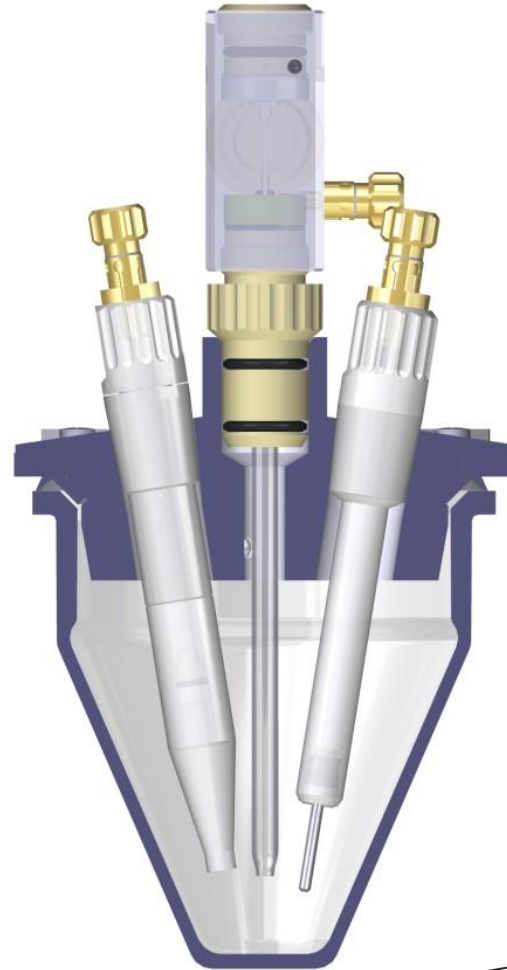
1 sensor combining:

- Working electrode
- Auxiliary electrode
- Reference electrode

Combined sensor

Examples

- scTRACE Gold
- SPE (screen-printed electrode)



Screen-printed electrode



scTRACE Gold



Applications with the
scTRACE Gold

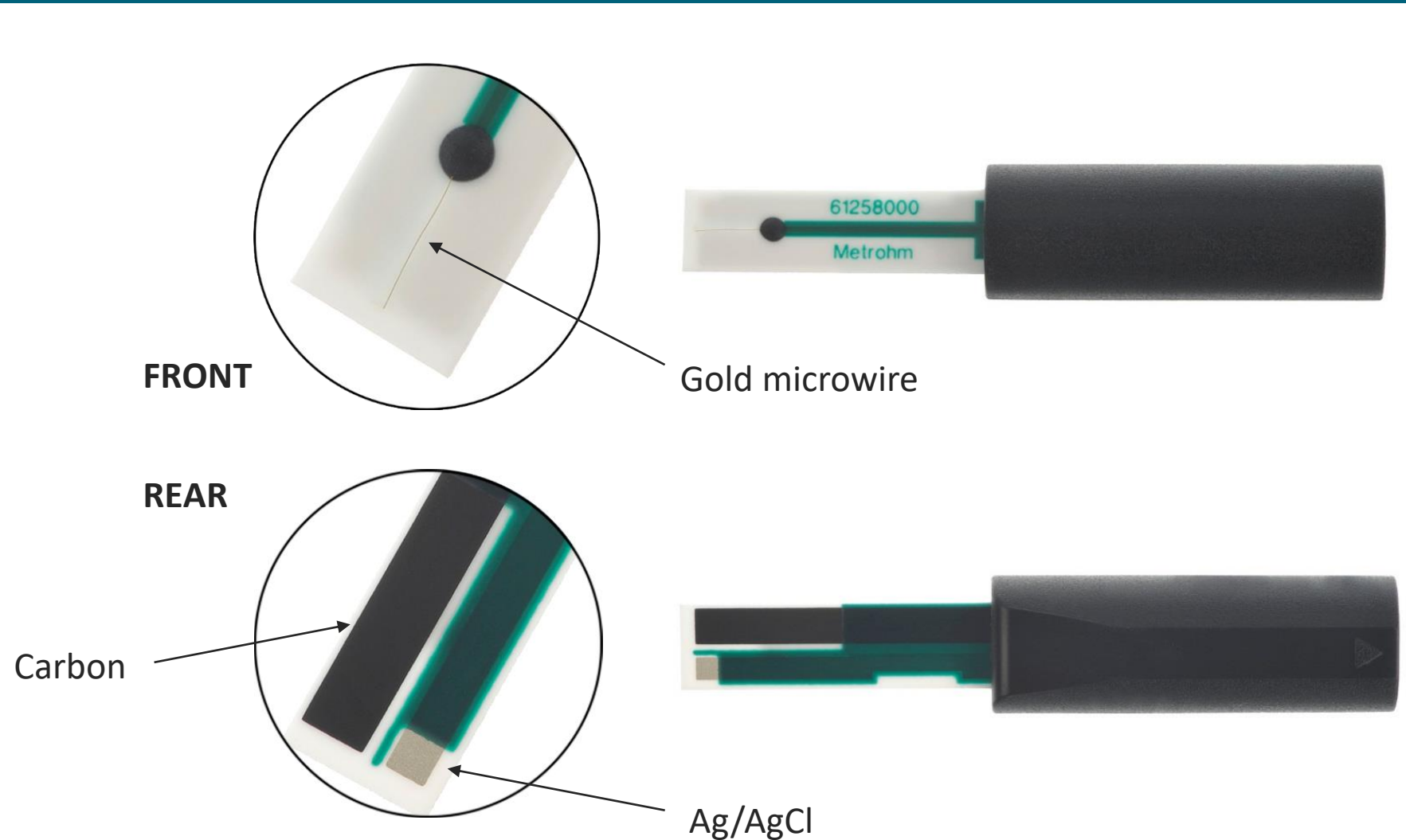
Front

- Working electrode: Gold microwire

scTRACE Gold

Rear

- AE: Carbon
- RE: Ag/AgCl



Pb in drinking water



Electrode

- scTRACE Gold (with Ag film)

Electrolyte

- $c(\text{citric acid}) = 0.045 \text{ mol/L}$
- $c(\text{KCl}) = 0.009 \text{ mol/L}$
- $c(\text{NaOH}) = 0.009 \text{ mol/L}$

Conditions

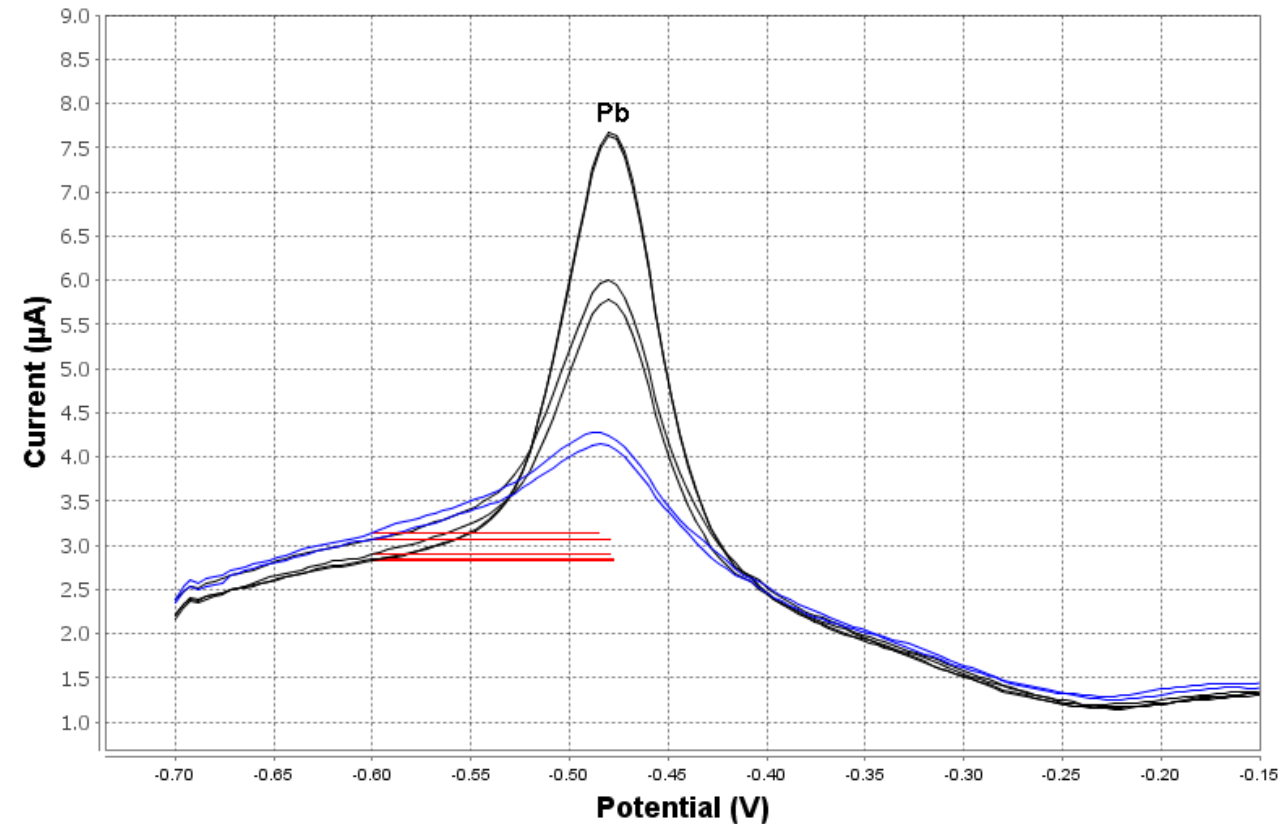
- Deposition: -0.7 V , 30 s
- Sweep: $-0.7 \text{ V} \dots -0.3 \text{ V}$

Sample size

- 15 mL

Result

- $\beta(\text{Pb}) = 2.8 \mu\text{g/L}$



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.



Application Bulletin 433
Application Note V-214

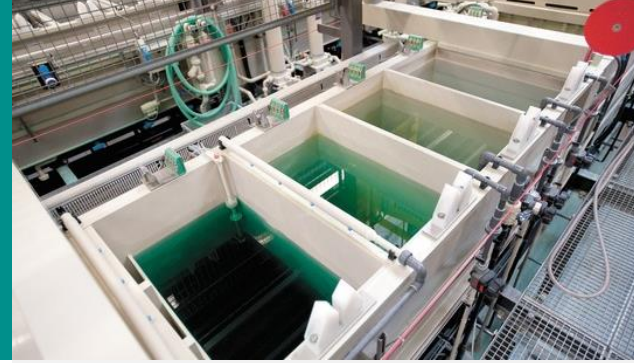
Detection limits in water according to WHO guidelines

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

- $c(\text{HCl}) = 0.1 \text{ mol/L}$

Conditions

- Deposition: -0.1 V , 30 s
- Sweep: $-0.2 \text{ V} \dots +0.3 \text{ V}$

Sample size

- 0.02 mL

Result

- $\beta(\text{Bi}) = 0.45 \text{ mg/L}$

Pb determination

Electrode

- scTRACE Gold (with Ag film)

Electrolyte

- $c(\text{citric acid}) = 0.045 \text{ mol/L}$
- $c(\text{KCl}) = 0.009 \text{ mol/L}$
- $c(\text{NaOH}) = 0.009 \text{ mol/L}$

Conditions

- Deposition: -0.7 V , 30 s
- Sweep: $-0.7 \text{ V} \dots -0.3 \text{ V}$

Sample size

- 0.05 mL

Result

- $\beta(\text{Pb}) = 0.9 \text{ mg/L}$



Applications with carbon
screen-printed electrodes

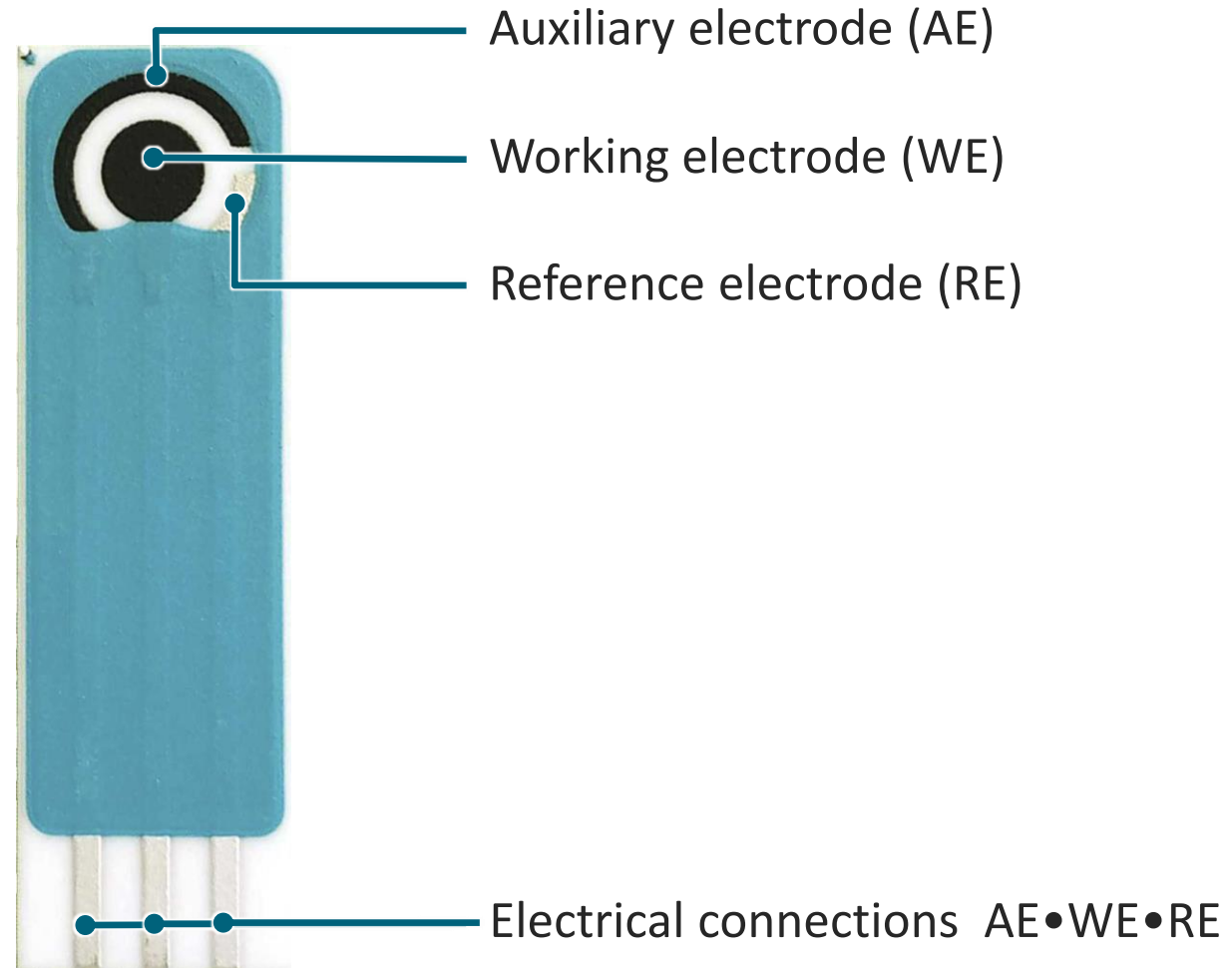
Screen-printed electrode

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

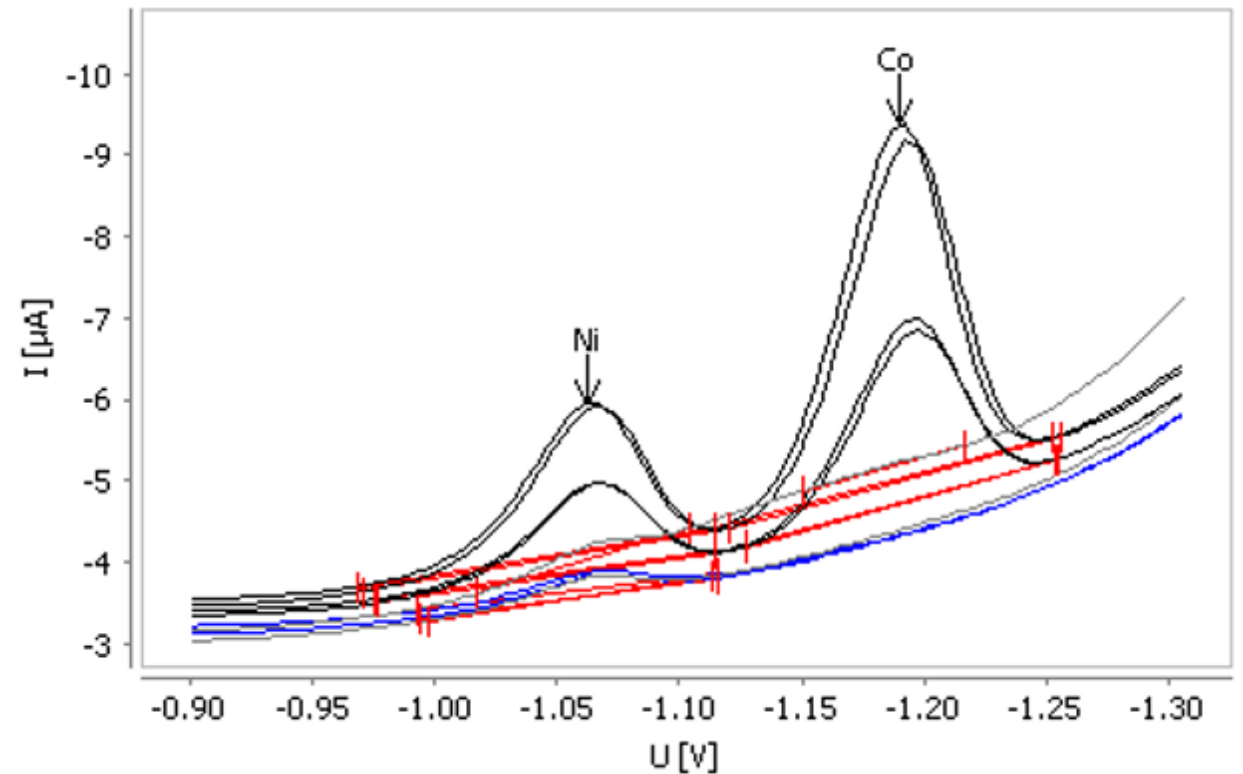
- Deposition: -0.9 V, 30 s
- Sweep: -0.9 V ... -1.3 V

Sample Size

- 10 ml or 15 ml

Result

- $B(\text{Ni}) = 0.56 \mu\text{g/L}$
- $B(\text{Co}) = -$



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




VA APPLICATION NOTE V-232

Nickel and cobalt in drinking water

Simultaneous determination in low µg/L range on the 11L screen-printed electrodes modified with a bismuth film

In the EU the legislation specifies 20 µg/L as the limit value for nickel in drinking water. The current provisional guideline value for Ni in the World Health Organization's «Guidelines for Drinking-water Quality» is set to a maximum concentration of 70 µg/L. The adsorptive stripping voltammetry (AdSV) technique performed on the ex-situ bismuth film modified Metrohm DropSens screen-printed electrode can be used to simultaneously detect concentrations as low as 0.4 µg/L for nickel and 0.2 µg/L for cobalt with 30 s deposition time. These limits can be lower further by increasing the deposition time. Another advantage of this method lies in the innovative and cost-effective screen-printed electrode. It is a combined sensor consisting of a carbon working electrode, Ag/AgCl reference, and carbon auxiliary electrode on a ceramic substrate. The disposable sensor does not need maintenance such as mechanical polishing or mechanical cleaning. It can be used conventionally in the laboratory with the 884 Professional VA, or alternatively in the field with the 946 Portable VA Analyzer. This method is best suited for manual systems.

www.metrohm.com 

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

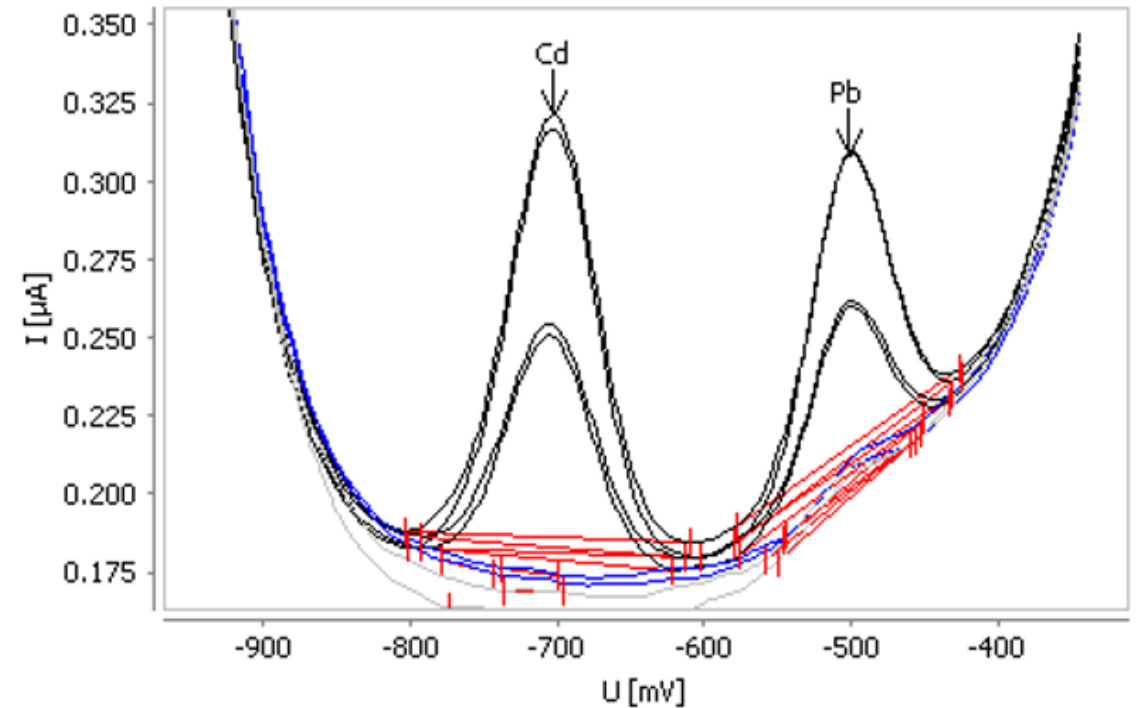
- $c(\text{acetic acid}) = 2 \text{ mol/L}$
- $c(\text{NH}_3) = 1 \text{ mol/L}$

Conditions

- Differential pulse
- Deposition: -1.1 V (60 s)
- Sweep: $-1 \text{ V} \dots -0.35 \text{ V}$

Result

- $\beta(\text{Cd}) = < \text{LOD}$
- $\beta(\text{Pb}) = < \text{LOD}$



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



VA APPLICATION NOTE V-221

Cadmium and lead in drinking water

Simultaneous determination by voltammetry using a Bi drop electrode

To reduce the toxic effects of cadmium on the kidneys, the skeleton, and the respiratory system, as well as to limit the neurotoxic effects of lead, the provisional guideline values in the World Health Organization's «Guidelines for Drinking-water Quality» are set to a maximum concentration of 3 µg/L for cadmium and 10 µg/L for lead in drinking water.

The completely mercury-free Bi drop electrode takes the next step towards converting voltammetric analysis into a non-toxic approach for heavy metal detection. Using this environmentally friendly sensor for anodic stripping voltammetry (ASV) allows the simultaneous determination of cadmium and lead in drinking water. With a 60 s deposition time, a limit of detection (LOD) of 0.1 µg/L for Cd and 0.5 µg/L for Pb can be reached. This outstanding sensitivity is more than sufficient to monitor the provisional WHO guideline values.

This method is best suited for automated systems or process analyzers, allowing the fully automatic determination of cadmium and lead in large sample series.

www.metrohm.com 

Application Bulletin 438/1
Application Note AN V- 221

Cd and Pb determination

RECOVERY

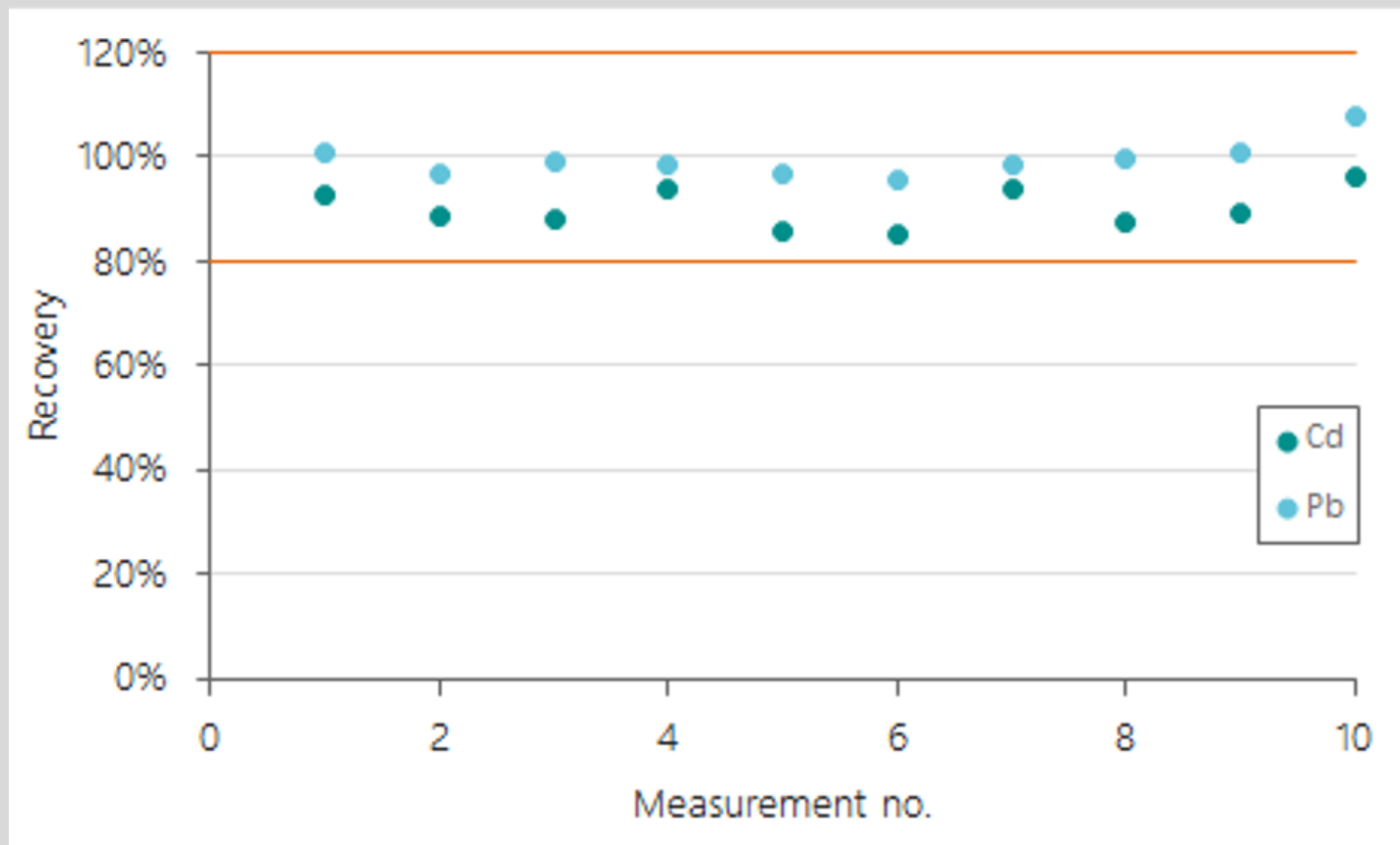
$\beta(\text{Cd}) = 1 \mu\text{g/L}: 90.2\%$

$\beta(\text{Pb}) = 5 \mu\text{g/L}: 99.5\%$

REPEATABILITY (RSD)

Cd: $\pm 4\%$

Pb: $\pm 3\%$



Application documents for Bi drop electrode



VA APPLICATION NOTE V-221

Cadmium and lead in drinking water

Simultaneous determination by voltammetry using a Bi drop electrode

To reduce the toxic effects of cadmium on the kidneys, the salivary, and the respiratory system, as well as to limit the neurotoxic effects of lead, the provisional guideline values in the World Health Organization's "Guidelines for Drinking-water Quality" are set to a maximum concentration of 2 µg/L for cadmium and 10 µg/L for lead in drinking water.

The completely mercury-free Bi drop electrode takes the next step towards converting voltammetric analysis into a non-toxic approach for heavy metal detection. Using this environmentally friendly sensor for anodic stripping voltammetry (ASV) allows the simultaneous determination of cadmium and lead in drinking water. With a 60 s deposition time, a limit of detection (LOD) of 0.1 µg/L for Cd and 0.5 µg/L for Pb can be reached. This outstanding sensitivity is more than sufficient to monitor the provisional WHO guideline values.

This method is best suited for automated systems or process analyzers, allowing the fully automatic determination of cadmium and lead in large sample series.

www.metrohm.com



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

The presence of iron in drinking water can lead to an unpleasant, harsh metallic taste or reddish-brown stains. In addition, iron bacteria which can grow in waters containing Fe at low (0.1 mg/L), create a reddish-brown slime that can clog plumbing and cause an offensive odor. Over a longer period, the formation of insoluble iron deposits is problematic in many industrial and agricultural applications, such as water supply, system cooling, or field irrigation. To avoid these problems, the U.S. Environmental Protection Agency (EPA) defines the Secondary Maximum Contaminant Level (SMCL) for water treatment and processing plants as 0.3 mg/L Fe in drinking water.

The voltammetric determination of the iron triethanolamine complex on the non-toxic Bi drop electrode does not require enrichment. This system uses catalytic signal enhancement, allowing both the detection at very low levels (limit of detection of 0.005 mg/L) and measurements in a wide range of concentrations up to 0.5 mg/L. This method is best suited for automated systems or process analyzers, allowing fully automatic determination of iron in a large sample series.

www.metrohm.com



VA APPLICATION NOTE V-223

Nickel and cobalt in drinking water

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

The main sources of nickel pollution are electroplating, metallurgical operations, or leaching from pipes and fittings. Catalysts for the petroleum and chemical industries are major pollution fields for cobalt. In both cases, the metals are either released directly, or via the waste water-river pathway into the drinking water system. Therefore in the EU the legislation specifies 20 µg/L as the limit value for the Ni concentration in drinking water.

The simultaneous and straightforward determination of nickel and cobalt is based on adsorptive stripping voltammetry (ASV). The unique properties of the non-toxic Bi drop electrode combined with ASV results in an excellent performance in terms of sensitivity. The limit of detection for 30 s deposition time is approximately 0.2 µg/L for nickel and 0.1 µg/L for cobalt, and can be lowered further by increasing the deposition time. This method is best suited for automated systems or process analyzers, allowing fully automatic determination in large sample series.

www.metrohm.com



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

Application Bulletin 438/1

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

Summary

Reference Electrode	6.1345.010
Electrode vessel	6.1345.042
Electrode holder	6.1341.030

Overview

The Application Bulletin describes the following methods:

- Activation/cleaning of Bi drop electrode
- A new sensor needs to be activated first. The activation must be carried out prior to the first use, and whenever the sensor has not been used for more than 1 hour. If the electrode needs to be cleaned either before, in between, or after determinations, the procedure described in the subchapter "Activation/cleaning of Bi drop electrodes" should be used.

Determination of cadmium and lead

Cadmium and lead are determined by anodic stripping voltammetry (ASV) using the non-toxic Bi drop electrode in a slightly acidic solution (pH 4.6). The Bi drop electrode is used here. With a deposition time of 60 s, the method is suitable for samples with [Cd] < 0.1 µg/L and [Pb] = 0.5–15 µg/L. The limit of detection is 0.1 µg/L for Cd and 0.5 µg/L for Pb. This method is best suited for tap water and mineral water samples.

Standard operating procedure

- Activation of the Bi drop electrode
- Determination of cadmium and lead in a blank or a check standard solution to validate electrode performance
- Determination of samples
- Rinsing of the Bi drop electrode with ultrapure water
- Dry storage in the storage vessel 6.2009.040

For more information about the standard operating procedure please refer to the comments in the chapters "Activation/cleaning of Bi drop electrodes" and "Comments at the end of this document."

Version: 2008E Page 1 of 6

Application Bulletin 439/1

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

Summary

Reference Electrode	6.0728.020
Electrode vessel	6.1345.010
Electrode holder	6.1341.040
Electrode holder	6.1341.020

Overview

The Application Bulletin describes the following methods:

- Activation/cleaning of the Bi drop electrode
- A new sensor needs to be activated first. The activation must be carried out prior to the first use, and whenever the sensor has not been used for more than 1 hour. If the electrode needs to be cleaned either before, in between, or after determinations, the procedure described in the subchapter "Activation/cleaning of the Bi drop electrodes" should be used.

Determination of iron

In an alkaline electrolyte (pH 10), the Fe(III) ions are directly reduced at the surface of the Bi drop electrode to Fe(II). The analytical signal is enhanced by the presence of K3C6H5 which reduces the reduced Fe(II) to Fe(0). The triethanolamine in the electrolyte prevents the formation and precipitation of Fe(OH)3 hydroxides in the alkaline measuring solution.

Standard operating procedure

- Activation of the Bi drop electrode
- Determination of cadmium and lead in a blank or a check standard solution to validate electrode performance
- Determination of samples
- Rinsing of the Bi drop electrode with ultrapure water
- Dry storage in the storage vessel 6.2009.040

For more information about the standard operating procedure please refer to the comments in the chapters "Activation/cleaning of the Bi drop electrode" and "Comments at the end of this document."

Version: 2008E Page 1 of 5

Application Bulletin 440/1

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

Summary

Cobalt is an essential element for humans because it is a component of vitamin B12. While small amounts of cobalt compounds are only slightly toxic to humans, larger doses from 25–50 mg per day may lead to skin, lung, and stomach diseases, as well as liver, heart, and kidney damage, and even cancerous growth. The same is valid for nickel, which can lead to inflammation at higher concentrations. Drinking a large amount of water containing nickel can cause discomfort and nausea. In the EU the legislation specifies 0.2 µg/L as the limit value for the Ni concentration in drinking water.

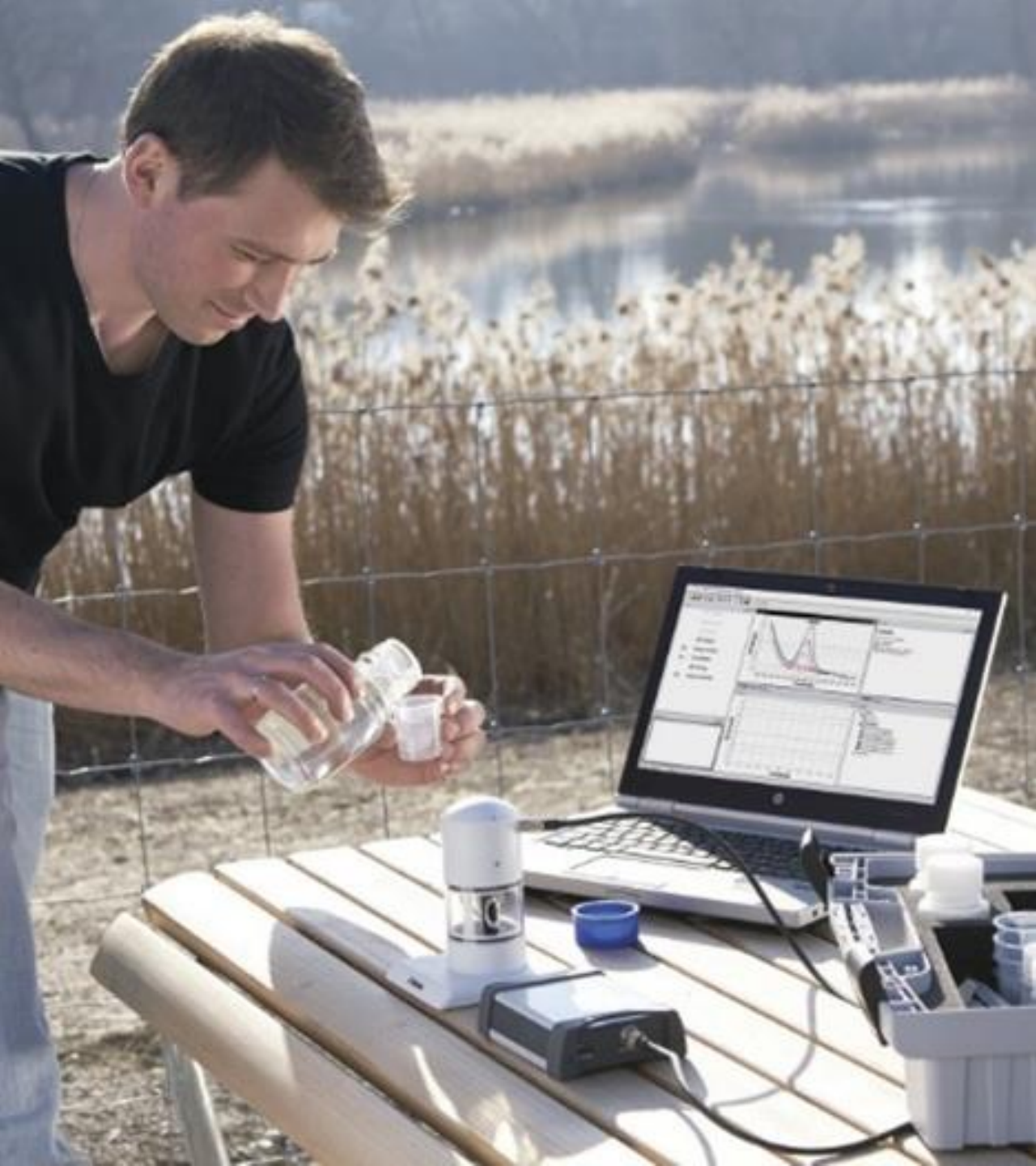
The simultaneous and straightforward determination of nickel and cobalt is based on adsorptive stripping voltammetry (ASV) using dimethylglyoxime (DMG) as a complexing agent in an alkaline electrolyte (pH 10). This method can be successfully applied to tap water, mineral water, and sea water samples using the Bi drop electrode. The limit of detection for 30 s deposition time is approximately 0.2 µg/L for nickel and 0.1 µg/L for cobalt, and can be lowered further by increasing the deposition time. With 30 s deposition time the maximum concentration of the best range of the method is 15 µg/L for Ni and 10 µg/L for Co, allowing the determination of Ni and Co concentrations between 0.2–15 µg/L and 0.2–10 µg/L, respectively.

Standard operating procedure

- Activation of the Bi drop electrode
- Determination of nickel and cobalt in a blank or a check standard solution to validate electrode performance
- Determination of samples
- Rinsing of the Bi drop electrode with ultrapure water
- Dry storage in the storage vessel 6.2009.040

For more information about the standard operating procedure please refer to the comments in the chapters "Activation/cleaning of Bi drop electrodes" and "Comments at the end of this document."

Version: 2008E Page 1 of 5



Implementation

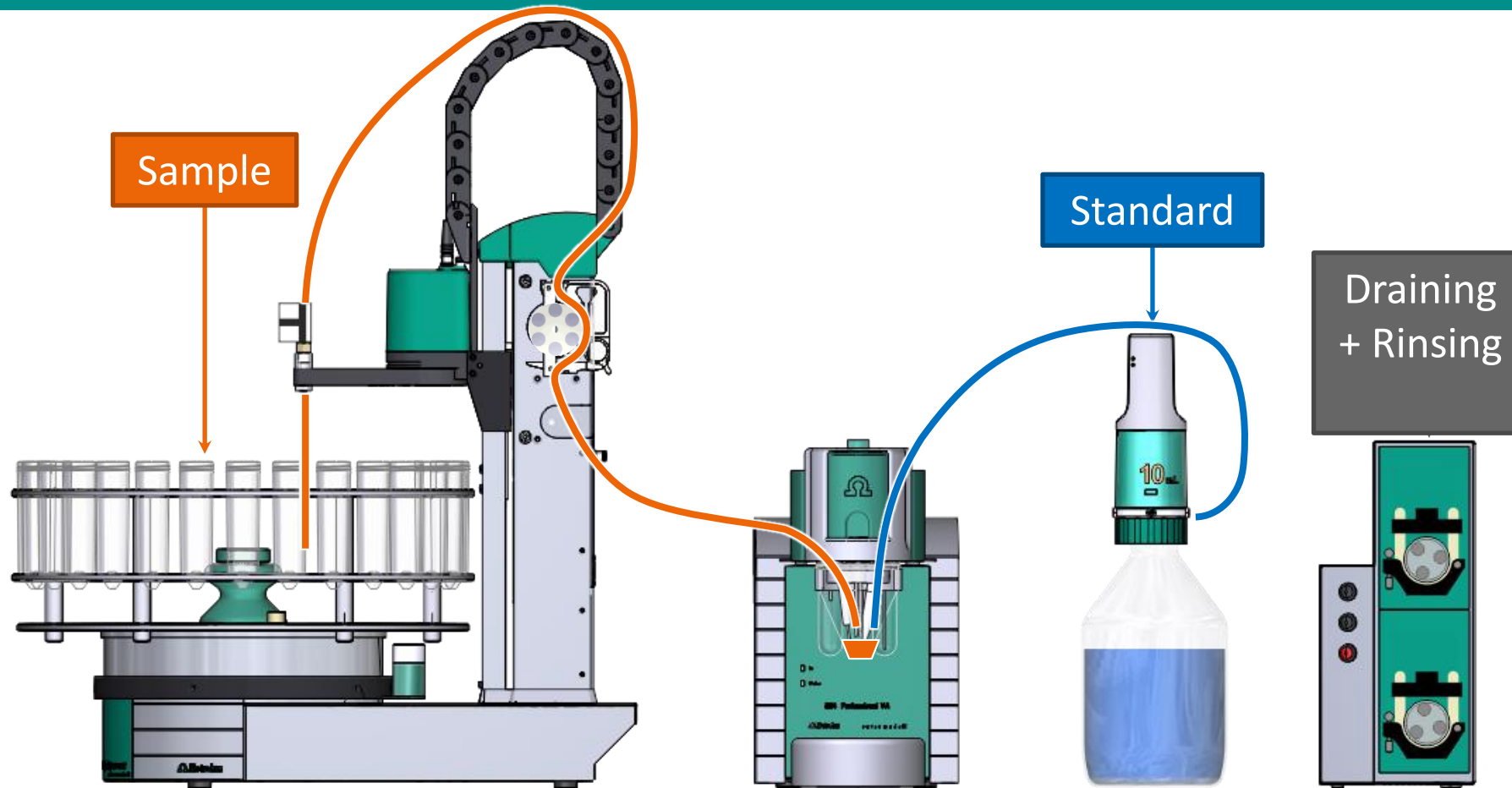
Field Measurements

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?

kia.williams@metrohmusa.com