Green Alternative Methods for Voltammetric Analysis in Different Water Matrices

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Stripping voltammetry uses electrochemical sensors for the determination of heavy metal ions in different types of samples. These can include boiler feed water, drinking water, sea water, beverages, and even industrial samples like plating baths.

Low detection limits (between µg/L and ng/L), the possibility to distinguish between different oxidation states (e.g., As(V) and As(III)) as well as between free and bound metal ions, and low costs of ownership combined with quick results (approximately 10-15 minutes) make stripping voltammetry attractive for both stationary and mobile applications.

To meet legal regulations and to eliminate the use of metallic mercury (Hg), Metrohm has developed Hg-free alternatives for heavy metal determination. An overview of these alternative methods is given in this article.

scTRACE Gold electrode

Glassy carbon electrode

Screen-printed electrode 11L

Bismuth drop electrode

Why mercury-free?

The term 'mercury-free' means that no metallic mercury is used in the analysis. In fact, for several years, the hanging mercury drop electrode (HMDE) was used extensively for voltammetric determination of heavy metals [1]. The mercury electrode is ideally suited for trace metal determination due to its high sensitivity, wide cathodic polarisation range, and the automatically renewable and reproducible electrode surface [2].

Despite its unique properties for electroanalysis, mercury is toxic and can accumulate in living organisms. To reduce the detrimental effect of metallic mercury on the environment and to replace it during the voltammetric determination of heavy metals, Hg-free sensors are required.

Overview of mercury-free applications

Recently, Metrohm has taken great efforts to combat the challenges related to the replacement of Hg in the voltammetric determination of heavy metals. These efforts led to the development of the following four new mercury-free sensors:

- scTRACE Gold electrode
- 11L carbon screen-printed electrode
- glassy carbon electrode
- bismuth drop electrode

Figure 1 shows an overview of the methods available for mercury-free determination of 16 heavy metals, along with corresponding limits of detection, for both the 884 Professional VA and the 946 Portable VA Analyser. These detection limits were determined in ultrapure water with different deposition times.

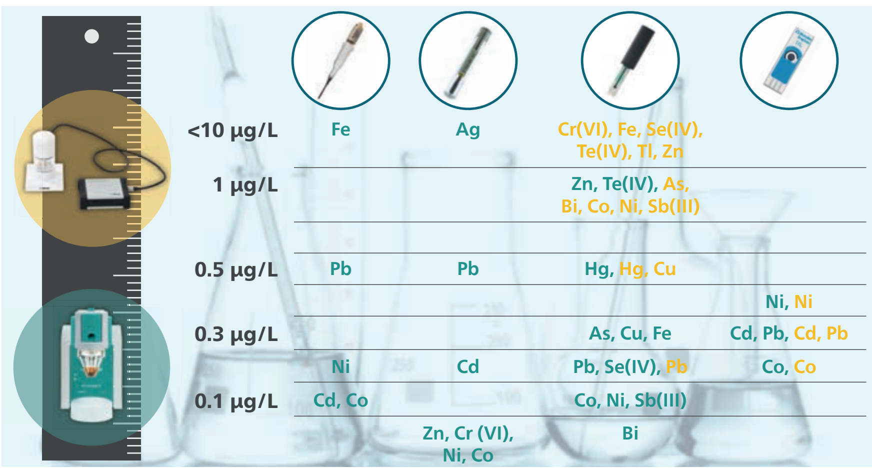

Figure 1. Overview of available methods for determination of heavy metals in purified water with different sensors and with corresponding limits of detection.

The limit of detection for most of these analytes is in the range of 0.1–0.5 µg/L when the 884 Professional VA is used. If the 946 Portable VA Analyser is used, then 15 heavy metals from Figure 1 can be determined, and the detection limit for the majority of them lies between 1–10 µg/L.

In the following sections, various application examples of Hg-free VA analysis of heavy metals in various water matrices will be presented and discussed.

Ultrapure and boiler feed water

Purified water is used during the production of myriad items like pharmaceuticals and semiconductors. It is also used for other industrial purposes, such as in thermal power plants. This example will cover details about the application of heavy metal determination in boiler feed water.

All thermal power plants use water for cooling and steam generation. Only extremely pure water guarantees efficient and trouble-free operation of these processes. Monitoring the water quality is therefore crucially important in these situations. Heavy metals such as copper or iron act as important corrosion indicators and can reflect potential safety issues. To facilitate trouble-free operation of power plants, various guidelines for boiler feed water have been established [3]. The guideline values for both copper and iron are in the low µg/L range (between 10 µg/L and 50 µg/L).

Stripping voltammetry can be employed for the sensitive determination of very low concentrations of heavy metals in boiler feed water. Concentrations down to approximately 0.3 µg/L can be determined for both copper and iron using the mercury-free scTRACE Gold sensor. In Figure 2, examples for the copper and iron determination in deionised water are presented.

Table 1. Results for the analysis of deionised water sample containing 1.0 µg/L Cu and 2.0 µg/L Fe, respectively.

Sample	Deionized water (spiked)
Sample size	10.0 mL
β(Cu)	1.0 µg/L
β(Fe)	2.0 µg/L

Drinking water

Drinking water is defined as water that is used for drinking purposes or food preparation, including both tap water and mineral water. Safe drinking water must not present any significant risks to human health over a lifetime of its consumption. The term 'safe' is defined by legal entities and includes limit values for physical and chemical parameters like the concentration of heavy metals, organic compounds, total suspended solids, and more. Due to the detrimental impact of heavy metals on human health, legal entities including the European Union (EU) and the US Environmental

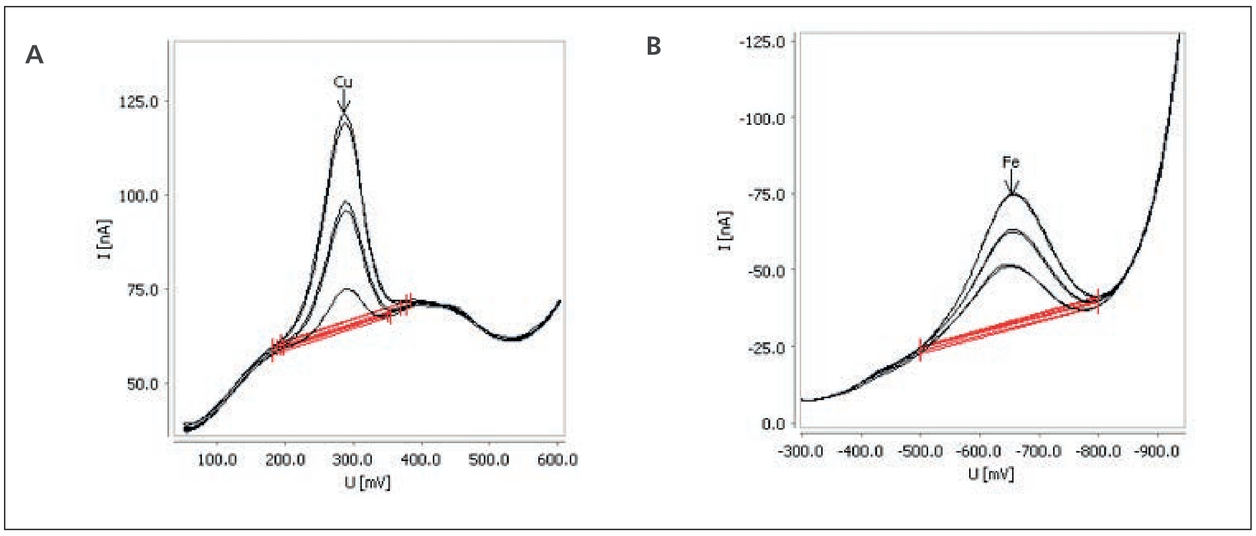

Figure 2. Determination of copper (A) and iron (B) in deionised water with the 884 Professional VA and 30 s deposition time.

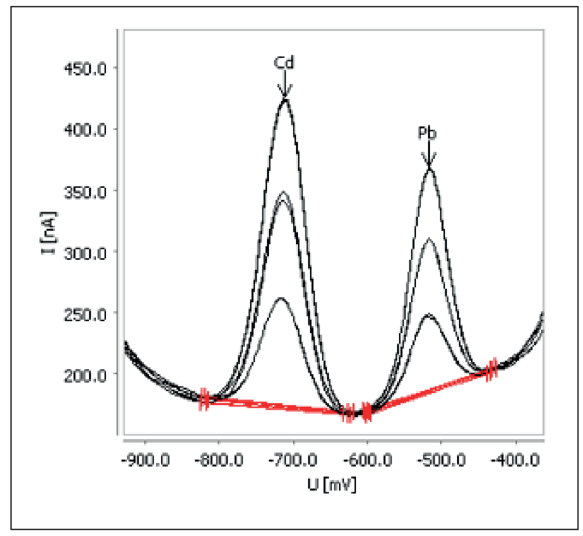

Figure 3. Example for determination of cadmium and lead in tap water sample containing 2 µg/L of each element.

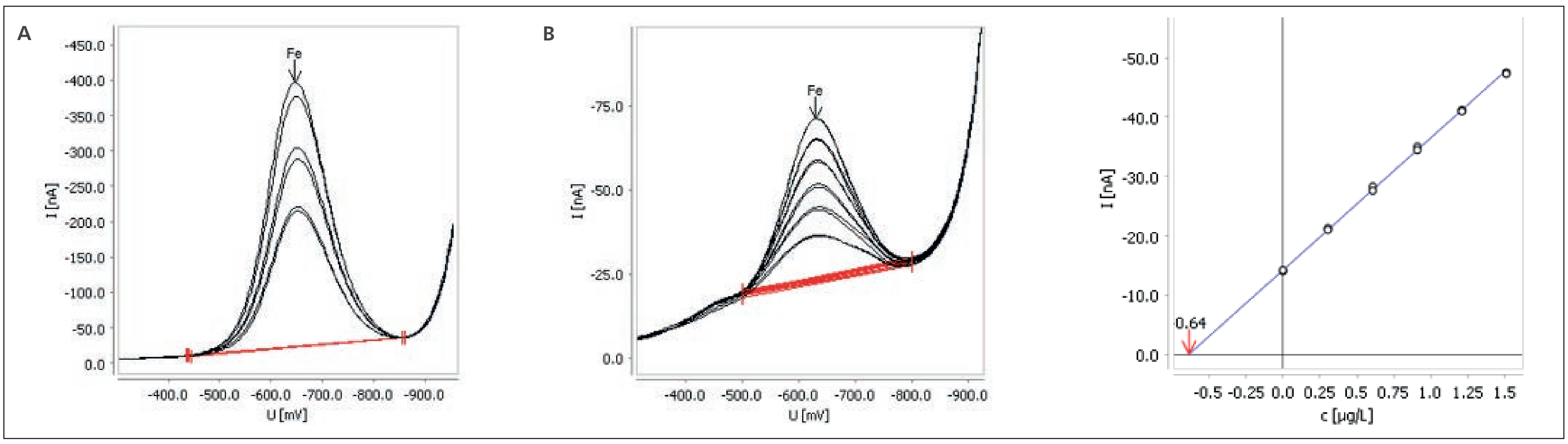

Figure 4. Example for (A) iron determination in an artificial sea water sample β(Fe) = 23.3 µg/L and for (B) a calibration curve in a low µg/L range.

Protection Agency (EPA) have established limit values for heavy metals in drinking water. However, in some countries there are no limit values for drinking water set by the local authorities. To assist in such situations, the World Health Organization (WHO) has defined certain guideline values. In the WHO's 'Guidelines for Drinking-water Quality', limits for organic, inorganic, radiological, microbiological, and additional parameters are set. For instance, the guideline concentration value for cadmium is set at 3 µg/L, and 10 µg/L for lead [4]. To monitor the limit and guideline values, sensitive analytical methods are required.

Metrohm provides anodic stripping voltammetry-based (ASV) methods that are suitable to monitor down to the WHO guideline values for multiple heavy metals in drinking water. One of the available methods employs the Bi drop electrode to simultaneously determine concentrations as low as 0.5 µg/L for lead and 0.1 µg/L for cadmium. An example of a tap water sample containing 2 µg/L cadmium and lead is shown in *Figure 3*.

Table 2. Results for the analysis of tap water sample containing 2.0 µg/L Cd and 2.0 µg/L Pb.

Sample	Cd (µg/L)	Pb (µg/L)
Tap Water	2.0	2.0

The main advantage of using this ASV method is the innovative and cost-efficient sensor: the Bi drop electrode. With this mercury-free sensor, concentrations in the low µg/L and even ng/L range can be reliably measured. The Bi drop electrode benefits users with its high stability and long lifetime. Its optimal performance is easily reached in a fully automated system when used for sample series in the laboratory environment.

Sea water

Sodium and chloride, along with magnesium, sulphate, calcium, potassium, bromide, and carbonate, represent more than 99% of the ions dissolved in sea water. Apart from these ions, there are more than 50 other naturally occurring elements in sea water. In many cases, they are present in trace concentrations. However, their low concentrations do not correlate well with their importance to the ecosystem. A good example of this concept is iron. The oceanic concentration of iron is extremely low due to its poor solubility and its biological uptake. It is one of the bioactive elements and is essential for marine organisms. The iron concentration in sea water significantly affects the ecosystem and controls the growth of microorganisms, as it is a micronutrient. Due to its trace concentrations, the determination of total dissolved iron in sea water requires a highly sensitive analytical approach.

The concentration of total iron in sea water can be determined using adsorptive stripping voltammetry (AdSV) with 2,3-dihydroxynaphthalene (DHN) as a complexing agent. Iron can be determined down to approximately 0.3 µg/L with this method using the mercury-free scTRACE Gold sensor. An example showing the iron determination in an artificial sea water sample is presented in *Figure 4*. In addition to iron, also nickel, cobalt, chromium (VI), cadmium, lead, antimony (III), thallium, and zinc can be determined with mercury-free sensors in sea water samples.

The AdSV method is simple to perform, specific, and free of interferences. It is a viable, less sophisticated alternative to atomic absorption spectroscopy (AAS) or inductively coupled plasma (ICP), requiring only a moderate investment in hardware and low running costs. However, the main advantage of this analytical method lies in the innovative and cost-effective sensing platform. The scTRACE Gold is a combined sensor consisting of a small gold wire working electrode, Ag/AgCl reference, and carbon auxiliary electrode on a ceramic substrate. The semi-disposable sensor does not require 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 and semiautomated systems.

Summary

This article has presented an overview of several mercury-free methods for the voltammetric determination of heavy metals in aqueous samples along with some specific application examples. Due to the accumulation step applied during the voltammetric determination, the sensitivity increases significantly. As a result, the limit values for heavy metal concentrations in different types of water samples defined by legal entities or guideline values recommended by WHO can be easily monitored. Problems resulting from the use of metallic mercury no longer play a role as Hg-free methods for the determination of 16 heavy metals are now available. Four different 'green' sensors, such as the scTRACE Gold, screen-printed electrodes, the glassy carbon electrode, and the Bi drop electrode can be used to determine low concentrations of heavy metals in different sample matrices, such as boiler feed water, drinking water, and sea water.

References

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