

From the Field to the Lab: Trace Metal Analysis of Drinking Water with Solid-State Electrodes

J. Gandhi¹, Alyson Lanciki², Jakub Tymoczko², Barbara Zumbrägel², Kia Williams¹

Summary

Heavy metals found in drinking water have been responsible for many illnesses on a global scale. Electrochemical (EC) methods have been developed to detect trace amounts of heavy metals in drinking water. However, the need for mercury in traditional EC methods prevents wide-spread adaptation due to environmental concerns. Solid-state electrodes present a solution by quickly and efficiently determining heavy metals at trace levels without the use of mercury. In this discussion, we will present voltammetric methods for trace metal determination using bismuth and gold in alternative solid-state electrodes in both laboratory and field conditions.

Introduction

The high level of sensitivity and straightforward setup of voltammetry makes it a valuable tool in drinking water analysis, but the use of mercury electrodes inhibits wide scale adaptation of the technique. The need for heavy metal ion determination in the field, sensor costs, and environmental issues are the main triggers for research on new sensors in voltammetry. Non-toxic and inexpensive materials are preferred for new sensors. The properties of these materials, however, can lead to some restrictions. First is the limited number of elements that can be detected on a particular electrode material (e.g., gold, carbon or bismuth). In addition, it is difficult to determine several elements simultaneously at the same mercury-free sensor. The choice of the most suitable electrode material, in combination with the optimum sensor design, helps to overcome these issues.

Bismuth-based electrodes prepared as both in-situ and ex-situ films on solid-state electrodes have been growing in popularity over the last twenty years. The broad electrochemical window and low toxicity of bismuth were key factors. In addition, bismuth can form alloys with a high number of heavy metals, and it exhibits high hydrogen overpotential, similar to mercury. These properties are particularly interesting for stripping voltammetry. The hydrogen evolution is suppressed efficiently while noise-free measurements at negative potentials can be carried out. While electrodes based on bismuth films are a good option, film deposition is an additional time-consuming step.

Gold electrodes have been used in electrochemistry for decades. However, the scTRACE Gold has a very special design that makes it uniquely suitable for drinking water analysis. Originally developed to improve the voltammetric determination of arsenic, the electrode has also proven to be suitable for the determination of numerous other elements, such as copper, iron, lead, and even toxic chromium(VI).

Instrumentation



884 PROFESSIONAL VA

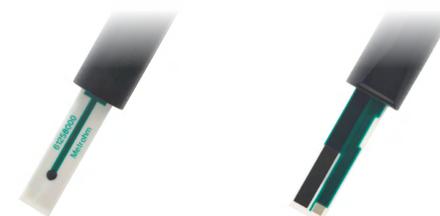


946 PORTABLE VA ANALYZER

Solid-state Electrodes



Bismuth drop working electrode



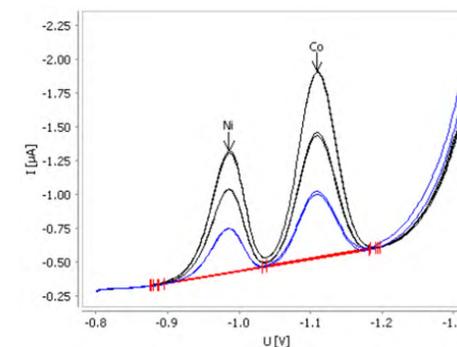
Close-up view of the gold micro-wire front working electrode on (left) and printed back reference and auxiliary electrodes on the scTRACE Gold.

SIMULTANEOUS Ni AND Co DETERMINATION WITH A BI DROP ELECTRODE

A tap water sample spiked with $\beta(\text{Ni}) = 0.5 \mu\text{g/L}$ and $\beta(\text{Co}) = 0.5 \mu\text{g/L}$ is pipetted into the measuring vessel. Ammonia/ammonium chloride buffer and the complexing agent dimethylglyoxime (DMG) are added, and the simultaneous determination of nickel and cobalt is carried out with an 884 Professional VA using the parameters specified below. The concentration is determined by two additions of a nickel and cobalt standard addition solution. The Bi drop electrode is electrochemically activated prior to the first determination

Mode:.....SQW-Square Wave
Deposition potential:.....-0.8 V
Deposition time:.....30 s
Start potential:.....-0.8 V
End potential:.....-1.3 V
Peak potential Ni:.....-0.97 V
Peak potential Co:.....-1.12 V

Results:Ni: 0.58 $\mu\text{g/L}$
Co: 0.54 $\mu\text{g/L}$



Results

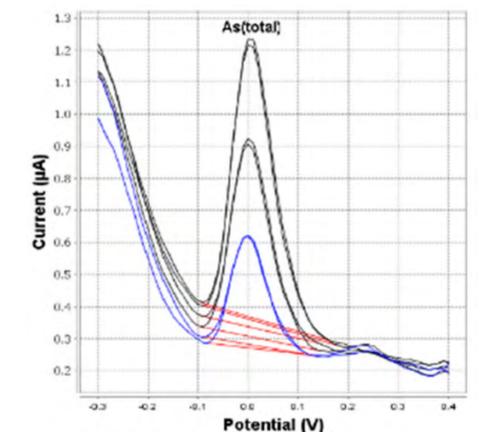
The simultaneous and straightforward determination of nickel and cobalt is based on adsorptive stripping voltammetry (AdSV). The unique properties of the non-toxic Bi drop electrode combined with AdSV results in an excellent performance in terms of sensitivity. The limit of detection for 30 s deposition time is approximately 0.2 $\mu\text{g/L}$ for nickel and 0.1 $\mu\text{g/L}$ for cobalt and can be lowered further by increasing the deposition time. The method is suitable for the determination of nickel and cobalt concentrations in water samples from $\beta(\text{Ni}^{2+}) = 0.2\text{--}8 \mu\text{g/L}$ and $\beta(\text{Co}^{2+}) = 0.1\text{--}10 \mu\text{g/L}$.

TOTAL ARSENIC IN MINERAL WATER ON A GOLD MICROWIRE ELECTRODE

The scTRACE Gold is electrochemically activated prior to the first determination. Then, the bottled mineral water sample and the supporting electrolyte are pipetted into the measuring vessel. The determination of arsenic is carried out with the 946 Portable VA Analyzer using the parameters specified below. The concentration is determined by two additions of an arsenic standard addition solution.

Mode:.....SQW-Square Wave
Deposition potential:.....-1 V
Deposition time:.....60 s
Start potential:.....-0.3 V
End potential:.....0.4 V
Peak potential As:.....0 V

Results:4.4 ($\mu\text{g/L}$)



Results

With a limit of detection (LOD) of 0.9 $\mu\text{g/L}$, anodic stripping voltammetry is a viable alternative to atomic absorption spectroscopy (AAS) for the determination of arsenic. 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 using the 946 Portable VA Analyzer with an scTrace Gold electrode.

References

- [1] Metrohm Application Note AN-V-223: Nickel and cobalt in drinking water-Simultaneous determination in the ng/L range on the Bi drop electrode
- [2] Application Bulletin 440: Determination of nickel and cobalt in water samples by adsorptive stripping voltammetry with a Bi drop electrode
- [3] Metrohm Application Note AN-V-210: Total arsenic in mineral water
- [4] Metrohm Application Bulletin 416: Determination of arsenic in water with the scTRACE Gold

¹Metrohm USA: jayesh.gandhi@metrohmusa.com

²Metrohm International Headquarters, CH-9100 Herisau/Switzerland