

Searching for trace

Round robin tests for trace analysis of heavy metals in drinking water

The little things are important

Trace analysis is becoming increasingly important. Contributing to that trend are ever tighter directives for maximum concentrations of contaminants. Regulations call for sensitive and reliable methods that can quantify minute amounts of substances harmful to human health and the environment.

The most commonly used techniques for such determinations are atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS). For electrochemically active substances, Metrohm offers an



es

inexpensive and simple solution: voltammetry. The method is part of various standards that regulate, among other things, the determination of a range of heavy metals in food and drugs, as well as in paints and coatings.

In recent years, the Metrohm subsidiary Metrohm Italiana has taken part in several nationwide round robin tests designed to evaluate the performance of the participating laboratories. In the tests, each laboratory determines the content of various metals in drinking water using a method of choice. Metrohm Italiana chose to perform the determinations

using voltammetry to prove the effectiveness, sensitivity, and accuracy of voltammetric methods.

«The most important foodstuff»

Water analyses play a critical role in process control and environmental analysis, as well as in food safety and elsewhere. In its first sentence, the DIN 2000 states that «Drinking water is the most important foodstuff; it cannot be replaced.» The DIN 2000 is the standard that defines the guiding principles for the drinking water supply in Germany. For obvious reasons, the quality of drinking water must be

ensured constantly. Mere traces of heavy metals pose a health hazard. Only high-performance analysis can ensure a low enough limit value – and test whether this limit value is being complied with. In addition to ICP and AAS, voltammetry can be used for the determination of trace concentrations. It combines high sensitivity and precision with manageable effort and costs, and is often used for validation purposes. The high element-specificity that is characteristic of voltammetry lends it a high tolerance of matrix influences – unlike spectroscopic methods. In addition, it can distinguish between various states of oxidation, for instance, between the trace element chromium(III), which is critical for life, and its carcinogenic cousin, chromium(VI).

Polarography, pulses, and precision

In voltammetry, concentrations are determined using current-voltage measurements. In the voltammetric measuring cell, there is a working electrode – traditionally a stationary electrode, but in polarography a mercury drop electrode – as well as a counter electrode and a third electrode used as a reference electrode (Figure 1). Voltage is applied to the working electrode to induce oxidation or reduction of the analyte. The resulting electrolytic current is recorded across a potential ramp. The current-voltage curve provides insight into the type and concentration of the dissolved substance.

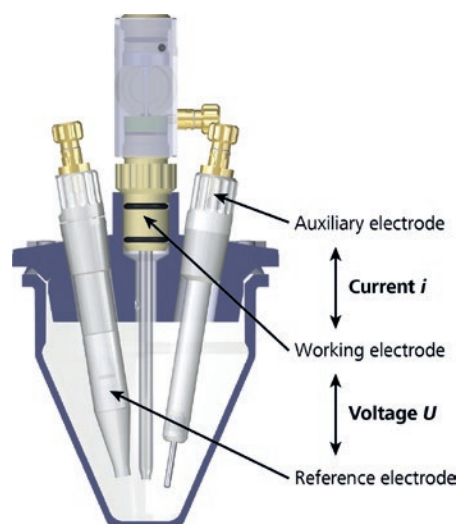


Figure 1. The electrode system of the voltammetric measuring cell consists of the auxiliary electrode, the working electrode, and the reference electrode. The current i is measured between the auxiliary electrode and the working electrode, while the voltage U is measured between the working electrode and the reference electrode.

Metrohm Italiana performs all of its measurements with stripping voltammetry. In stripping voltammetry the dissolved metal is deposited on the mercury electrode as either a metal or a complex when voltage is applied. Following a defined deposition time, a potential ramp is applied to the working electrode which causes the analyte to go back into solution.

At this point – and not during deposition – the current is measured and plotted against the voltage in a voltammogram for the purpose of quantification. Stripping voltammetry is more sensitive than conventional polarography because the measured currents are stronger as a result of the preceding deposition of the analyte.



Measurement precision can be further increased if, as is the case at Metrohm Italiana, a staircase potential ramp is used with brief potential pulses superimposed. Methods that use this type of potential ramp are referred to as differential pulse polarography, because the difference between two measuring points is recorded in the current-voltage curve instead of the individual measured values. The first measurement is taken before the pulse, and the second at the end of the pulse (Figure 2). This provides the differential of a conventional voltammetric measurement curve. A peak results in the voltammogram, the height of which is proportional to the concentration of the analyte. The limit of detection of differential pulse polarography is 10^{-7} to 10^{-8} mol/L.

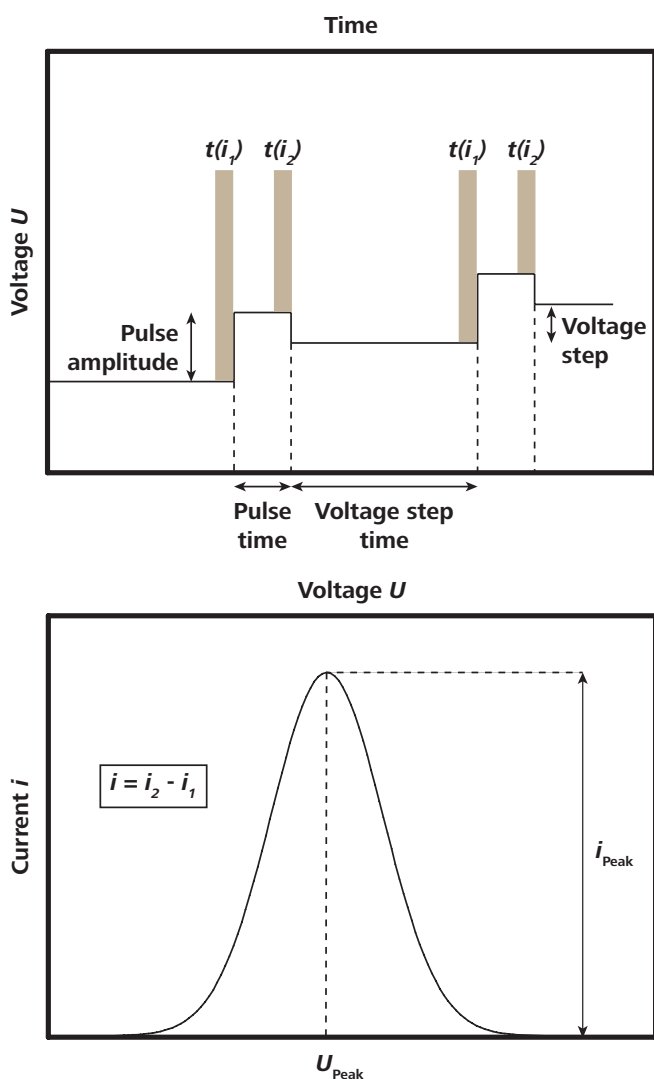


Figure 2. The pulse signal (top) and the current-voltage curve (bottom) in differential pulse polarography. The light brown bars mark the moments at which measurements are taken.

Results of the round robin test

A total of 428 laboratories participated in the round robin test. The participants determined concentrations of copper (Cu), iron (Fe), aluminum (Al), vanadium (V), zinc (Zn), chromium (Cr), manganese (Mn), lead (Pb), selenium (Se) and cadmium (Cd) in the spiked drinking water samples. The values were all within the range of the permissible limit values within the EU (Table 1). The most frequently used methods in the round robin tests were AAS and ICP. The results that Metrohm Italiana obtained using the 797 VA Computrace and the Multi-Mode electrode in HMDE (hanging mercury drop electrode) mode reveal a close match with the mean values obtained by all of the participants (Figure 3). The laboratory thus performed very well in the round robin test. With a limit of detection in the ng/L-range (Table 1) and low associated costs and effort, voltammetry is an indispensable tool in trace analysis.

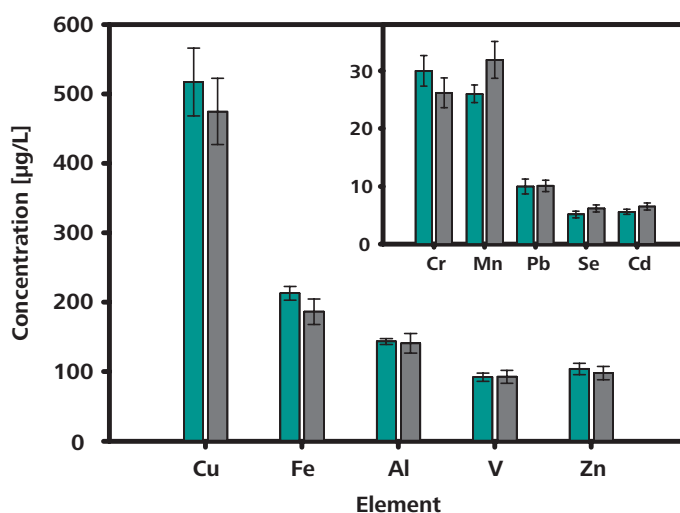


Figure 3. The turquoise colored bars depict the measured data from Metrohm Italiana. The mean values of measurements of all of the participating laboratories are depicted in gray. The error bars stand for the respective standard deviation.



Table 1. A selection of elements with their limits of detection by voltammetry (VA) as well as their EU limit values and WHO guideline values for concentrations in drinking water

| Element | Limit of detection (VA) | EU limit value | WHO guideline value |
|------------|-------------------------|----------------|---------------------|
| Antimony | 0.2 µg/L | 5 µg/L | 20 µg/L |
| Arsenic | 0.1 µg/L | 10 µg/L | 10 µg/L |
| Bismuth | 0.5 µg/L | – | – |
| Cadmium | 0.05 µg/L | 5 µg/L | 3 µg/L |
| Chromium | 0.025 µg/L | 50 µg/L | 50 µg/L |
| Cobalt | 0.05 µg/L | – | – |
| Copper | 0.05 µg/L | 2000 µg/L | 2000 µg/L |
| Iron | 0.05 µg/L | 200 µg/L | – |
| Lead | 0.05 µg/L | 10 µg/L | 10 µg/L |
| Mercury | 0.1 µg/L | 1 µg/L | 6 µg/L |
| Manganese | 2 µg/L | 50 µg/L | – |
| Molybdenum | 0.05 µg/L | – | – |
| Nickel | 0.050 µg/L | 20 µg/L | 70 µg/L |
| Platinum | 0.0001 µg/L | – | – |
| Rhodium | 0.0001 µg/L | – | – |
| Selenium | 0.3 µg/L | 10 µg/L | 10 µg/L |
| Thallium | 0.05 µg/L | – | – |
| Tungsten | 0.2 µg/L | – | – |
| Uranium | 0.025 µg/L | – | 30 µg/L |
| Zinc | 0.050 µg/L | – | – |

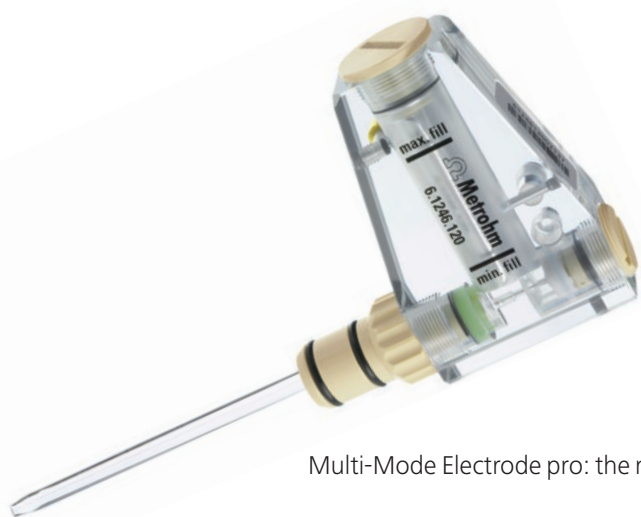
Further information

Standards

Metrohm works in accordance with standards: a range of ISO, DIN, and EPA standards describe voltammetric methods for trace analysis of heavy metals. The key standards are listed in Table 2.

Table 2. Standards describing methods for the voltammetric analysis of heavy metals

| Standards | |
|--------------------|---|
| ISO 713 | Zinc – Determination of lead and cadmium contents. Polarographic method. |
| ISO 3856-4 | Paints and varnishes – Determination of "soluble" metal content. Part 4. Determination of cadmium content. Flame atomic absorption spectrometric method and polarographic method. |
| ISO 6636-1 | Fruits, vegetables and derived products. Determination of zinc content. Part 1. Polarographic method. |
| EPA 7063 | Arsenic in aqueous samples and extracts by anodic stripping voltammetry (ASV) |
| EPA 7472 | Mercury in aqueous samples and extracts by anodic stripping voltammetry (ASV) |
| EPA 7198 | Cr(VI) in water by polarography |
| ASTM D 3557-02 | Standard Test Methods for Cadmium in Water |
| ASTM D 3559-03 | Standard Test Methods for Lead in Water |
| AOAC 968.16 | Fumaric acid in food. Polarographic method. |
| AOAC 972.24 | Lead in fish. Polarographic method. |
| AOAC 972.46 | Bismuth compounds in drugs |
| AOAC 979.17 | Lead in evaporated milk and fruit juice |
| DIN 38406, Part 16 | Determination of 7 metals (Zn, Cd, Pb, Cu, Tl, Ni, Co) by voltammetry in water |
| DIN 38406, Part 17 | Determination of uranium - method using adsorptive stripping voltammetry in surface water, raw water and drinking water |
| DIN 38413, Part 5 | EDTA and NTA in water samples |
| HMSO/Br.Dept. Env. | Metal ions in marine and other waters: Zn, Cd, Pb, Cu, V, Ni, Co, U, Al, Fe |



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