Water analysis in the field: Determining arsenic, mercury, and copper

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Heavy metals such as arsenic and mercury find their way into the ground water in many regions of the world, either through natural processes or as the result of human activities. Limit values are exceeded many times over, particularly for arsenic in drinking water, in many areas. This calls for a rigorous monitoring of water quality. The present whitepaper focuses on field determinations of arsenic, mercury, and copper – directly at the sampling site.

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Heavy metals in drinking water – a global problem

The contamination of drinking water with heavy metals is a global problem. A particularly prominent case is the highly arsenic-contaminated well water in Bangladesh, although it is by far not the only one. According to an estimate by the WHO, more than 200 million people worldwide are exposed to drinking water containing more than 10 µg/L arsenic and thus exceeding the WHO guideline value [1]. Large regions in the US, for example, are affected by elevated levels of arsenic resulting from geological conditions, including among them states in the Southwest such as Nevada, but also New England and the Upper Midwest [2]. In Switzerland as well, drinking water sources are used in scattered locations that have an arsenic content that exceeds the WHO guideline value [3].

The consequences of chronic arsenic poisoning are as serious as they are varied. Skin lesions and skin cancer as well as other types of cancers, disorders of the nervous system, heart attacks, and pulmonary tuberculosis are only a few examples.

How arsenic gets into drinking water

The contamination of ground water with arsenic is to a large extent caused by natural processes. River waters, for example, release arsenic from weathered rock. Arsenic deposits then in the sediments, preferentially in river deltas. If the sediments are in contact with ground water aquifers, the ground water becomes contaminated [4]. This the case, for example, at the world's largest river delta, the Ganges Delta in Bangladesh.

But this is not all: human activities can also cause increased arsenic concentrations in the environment. Particularly through contaminated wastewater and seepage in connection with mining and waste landfills, arsenic can find its way into ground water. There are new examples to be discovered to the present day, even in developed countries such as Germany and the US [5, 6]. This is why a monitoring of wastes, including waste waters, is needed here. Similarly, government agencies must check the arsenic concentrations in natural waters, particularly in the vicinity of such plants, at regular intervals.

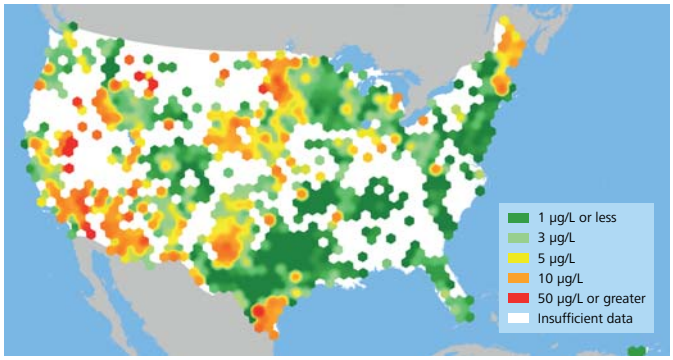

Figure 1. Distribution of arsenic in the ground water in the US. Shown here is the 75th percentile, in each case within a radius of 50 km. That means that the concentrations in the samples investigated within a range of 50 km were lower than the specified value in 75% of the cases – and higher in 25%. Figure: U.S. Geological Survey

Figure 2. Two Indian girls carry well water to their homes. While the construction of wells in the Ganges Delta region has reduced diseases caused by pathogen-contaminated surface water, a large number of these wells produce water that is strongly contaminated with arsenic. Chronic and acute arsenic poising that affect large parts of the population are the consequence.

Wood preservatives containing arsenic

Also problematic in a number of countries is the use of chromated copper arsenate (CCA) in wood preservation agents: arsenic seeps out of CCA-treated utility poles, pasture fences, and vineyard poles and into the ground. It is particularly the latter which can cause a considerable contamination of the soil and ground water due to the high density of poles per acre [7]. The use of CCA and CCA-treated wood has been forbidden in the EU since 2004 except in a small number of cases; it remains however widespread and widely accepted in the US, Australia, and New Zealand [8, 9].

Not all arsenic is the same

Arsenic is present in water in two oxidation states: in the form of the highly toxic arsenic(III) and in the form of the less toxic arsenic(V). It is therefore important not only to note the total concentration when determining arsenic; the speciation of the arsenic is also relevant to the rating of water quality. Because arsenic(III) is unstable and oxidizes spontaneously to form arsenic(V), determination of As(III) should be carried out onsite if possible, directly after sampling.

Figure 3. The Ganges Delta, as seen from an airplane. With a surface area of around 140 km^2, it is the largest river delta in the world. The arsenic-rich sediments of the Ganges Delta are the source of the high arsenic concentrations in Bangladesh's ground water.

Mercury: Input from natural and anthropogenic sources

In addition to arsenic, other heavy metals, including mercury, can find their way into drinking water and surface waters and cause harm there to humans as well as to the environment. Our planet continuously «breathes» out large quantities of mercury into the atmosphere through vegetation and the Earth's crust. Not only that, human activities are coming to play an ever larger role in the deposition of mercury in the atmosphere: In the 20th Century, the anthropogenic share of atmospheric mercury was around 70% – and increasing [10, 11]. For example, the burning of fossil fuels and small-scale gold mining are both paths for introducing mercury into the environment. Certain industrial processes are also problematic, in particular the manufacture of cement, metal refining, and chlor-alkali electrolysis following the amalgam process for the extraction of chlorine and caustic soda. Furthermore, just as is the case with arsenic, seepage water from waste landfills can also cause mercury contamination in ground water [12]. In the past, the use of mercury as a cheap fungicide in agriculture has also led to cases of poisoning among humans [13].

A part of the mercury that is released enters the waters through precipitation. It accumulates in the tissue of fish and crustaceans and thus becomes a hazard for humans: the consumption of contaminated fish introduces mercury into the human body. Due to its toxicity to both humans and the environment, the determination of mercury is mandatory to an equal extent in both waters which are fished and waters which are not fished.

Figure 4. Mercury leaches out of the waste at landfills and can seep into the ground and into ground water.

Figure 5. Mercury from the water accumulates in the tissue of fish and crustaceans. A diet rich in fish can therefore lead to increased exposure to mercury.

Figure 6. The Portable VA Analyzer enables onsite measurements and thus enables, for example, reliable speciation analyses of arsenic. The measuring instrument and the necessary accessories fit in the accompanying handy transport case.

Onsite determination of arsenic, mercury, and copper

Mercury, copper, total arsenic, and the concentrations of arsenic(III) and arsenic(V) can be determined voltammetrically onsite with the 946 Portable VA Analyzer. The portable analyzer is specially designed for the determination of traces of arsenic, mercury, and copper in water and is suitable for checking compliance with the respective WHO guideline values, as shown in Table 1.

The instrument, together with the accessories required for the measurement and the bottles for the reagents, fits in a handy case. Only a laptop is required in addition for control of the instrument. Measurements can be carried out very simply right at the sampling site, e.g., in the trunk of a car. This has not only the advantage of obtaining results quickly without having to transport the samples to a laboratory first. In the case of arsenic, the onsite measurement also makes it possible to obtain a reliable determination of the oxidation states. This would be flawed by the oxidation of the very unstable arsenic(III) if the sample must first be brought to a laboratory.

Table 1. WHO guideline values for arsenic, mercury, and copper in drinking water and the detection limits of the three heavy metals with the 946 Portable VA Analyzer.

Analyte	WHO guideline value	Detection limit Portable VA Analyzer
Arsenic	10 µg/L	1 µg/L
Mercury	6 µg/L	0.5 µg/L
Copper	2000 µg/L	0.5 µg/L

The measurement

Determination of heavy metals with the 946 Portable VA Analyzer is quick and convenient. After sampling, the sample and the electrolyte are filled into the measuring cell. Then the suitable method is selected and the measurement is started on the laptop, which makes operation of the 946 Portable VA Analyzers particularly simple. If necessary, some measuring parameters, e.g., the sample volume or the volume and the number of standard additions can be modified by the user. During the measurement, the software prompts the user at the correct points to perform the standard additions, which are pipetted into the measuring cell through the openings provided for that purpose. Finally, the software evaluates the result autonomously. PDF reports can be compiled either manually or automatically.

The 946 Portable VA Analyzer uses the unique scTRACE Gold senor for the measurement. This sensor combines the gold-microwire working electrode with the screen-printed reference and auxiliary electrodes. This offers several advantages over other electrodes: The scTRACE Gold is virtually maintenance-free, requires no tedious conditioning, and, if necessary, can simply be replaced at any time.

From sampling to the result in minutes

The determination of heavy metals in water is an important topic in environmental analysis around the world. With the Metrohm 946 Portable VA Analyzer, it is not only possible to determine total arsenic and the arsenic species, but also mercury and copper by voltammetry without leaving the sampling site. Field measurement permits faster data acquisition on the one hand and, on the other, prevents the results from being affected by chemical changes that occur after sampling, e.g., the oxidation of arsenic(III) to arsenic(V). Software and accessories, particularly the maintenance-free scTRACE Gold sensor, have been designed for exceptionally easy handling. This compact system therefore meets all the requirements for measuring in the field.

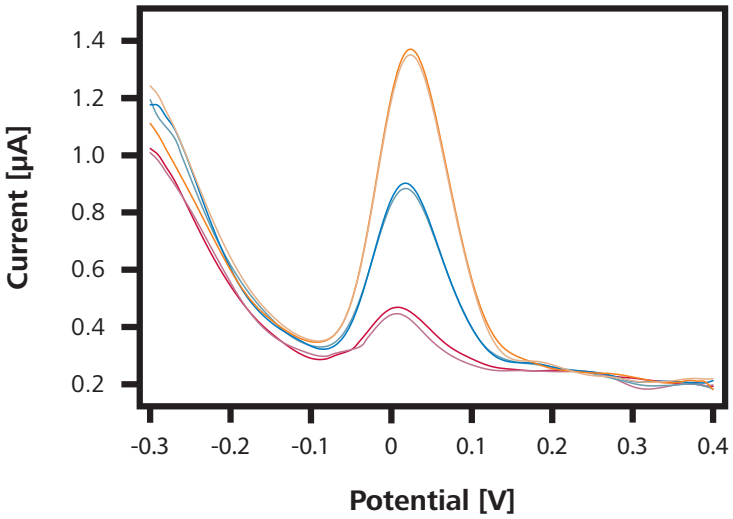

Figure 7. Current-voltage curve of an arsenic(III) determination in mineral water with the 946 Portable VA Analyzer with two standard additions of an As(III) standard solution.

References

[1] Naujokas, M. F.; Anderson, B.; Ahsan, H.; Aposhian, H. V.; Graziano, J. H.; Thompson, C.; Suk, W. A. (2013) The Broad Scope of Health Effects from Chronic Arsenic Exposure: Update on a Worldwide Public Health Problem. Environ. Health Perspect. 121:295–302

[2] Blum, D. (2014, October 30) A heart risk in drinking water. *Well Blog – The New York Times.* Retrieved from https://well.blogs.nytimes.com

[3] Pfeifer, H. R.; Zobrist, J. (2002) Arsenic in drinking water – also a problem in Switzerland? EAWAG news. 53:15–17

[4] Berg, M. (2002) Arsenic in drinking water – Vietnam, new focus of attention. EAWAG news. 53:12–14

[5] Kümmel, G. (2010, March 2) Arsen im Sickerwasser entdeckt. Main-Echo. Retrieved from http://www.main-echo.de/

[6] Reilly, A. (2017, March 23) Judge rules violated Clean Water Act with arsenic leak. E&E News. Retrieved from https://www.eenews.net

[7] Robinson, B.; Greven, M.; Green, S.; Sivakumaran, S.; Davidson, P.; Clothier, B. (2006) Leaching of copper, chromium and arsenic from treated vineyard posts in Marlborough, New Zealand. Sci. Total Environ. 364:113–123

[8] Overview of Wood Preservative Chemicals. US EPA *https://www.epa.gov/ingredients-used-pesticide-products/overview-wood-preservative-chemicals* (accessed June 26, 2017)

[9] McPhee, E. (2017, March 13) Vineyard posts a 'charcoal' grey area as council considers stockpile log. *The Marlborough Express.* Retrieved from *https://www.stuff.co.nz*

[10] Schuster, P. F.; Krabbenhoft, D. P.; Naftz, D. L.; Cecil, L. D.; Olson, M. L.; Dewild, J. F.; Susong, D. D.; Green, J. R.; Abbott, M. L. (2002) Atmospheric Mercury Deposition during the Last 270 Years: A Glacial Ice Core Record of Natural and Anthropogenic Sources. Environ. Sci. Technol. 36(11):2303–2310

[11] Kang, S.; Huang, J.; Wang, F.; Zhang, Q.; Zhang, Y.; Li, C.; Wang, L.; Chen, P.; Sharma, C. M.; Li, Q.; Sillanpää, M.; Hou, J.; Xu, B.; Guo, J.(2016) Atmospheric Mercury Depositional Chronology Reconstructed from Lake Sediments and Ice Core in the Himalayas and Tibetan Plateau. Environ. Sci. Technol. 50(6):2859–2869

[12] Sahli, M. (2016, February 26) Lonza muss bei Deponie-Schutz über die Bücher. *Schweizer Radio und Fernsehen.* Retrieved from https://www.srf.ch

[13] *Factsheet Quecksilber Juli 2012;* Bundesamt für Gesundheit BAG: Bern, Switzerland, 2012.

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