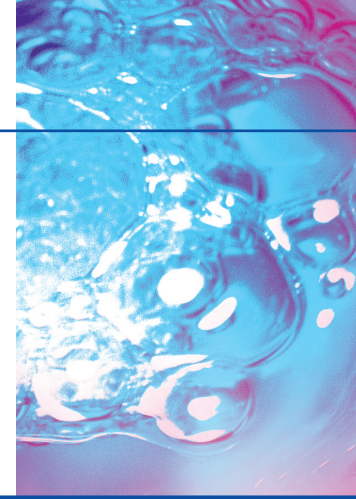


Heavy Metals, WATER AND HEALTH



**WATER/
Wastewater**

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Everyone involved in the environment and health knows that whilst traces of some heavy metals, copper and zinc for example, are essential to maintaining good health, in higher concentrations, even beneficial metals can be toxic. Heavy metals are absorbed from a variety of sources in the environment and accumulate in the body over time. Water supplies can be contaminated by human activity, such as the discarding of industrial and consumer waste into landfill sites. Of course, commercial processes – mining, agriculture and manufacturing, for example – are also common sources of heavy metals contamination. And acidic rainwater can cause metals to leach out of surrounding soil and rock to contaminate groundwater. A series of recent international initiatives signals new, more cohesive action to ensure environmental sustainability. Bodies involved include the World Health Organisation (WHO), and it is proposed to upgrade the United Nations Environment Program (UNEP) to become a UN specialised agency for the environment.

In this article, we outline some of the health issues associated with the toxicity of chromium and arsenic, and highlight the use of Anodic Stripping Voltammetry (ASV) techniques for the accurate, reliable and cost-effective measurement of these metals in water samples.

Impacting Health

Environmental factors are a root cause of a significant burden of death, disease and disability globally. The WHO estimates that the impact of poor water quality and access to clean water Richard – you might want to clarify that this means access to clean water, exposure to toxic elements, and degraded urban environments accounts for at least 25% of death and disease around the world (figure 1).

Against this background, exposure to heavy metals plays a significant role. Two of the most significant metals are arsenic and chromium.

Arsenic is a naturally occurring element widely distributed in the earth's crust. In the environment, it is combined with oxygen, chlorine, and sulphur to form inorganic arsenic compounds. In animals and plants, it combines with carbon and hydrogen to form organic arsenic compounds.

Breathing high levels of inorganic arsenic can result in a sore throat or irritated lungs and ingestion can be fatal. Lower levels can lead to nausea and vomiting, depression of red and white blood cell production, abnormal heart rhythms, blood vessel damage, and a sensation of "pins and needles" in the hands and feet. Ingesting or breathing low levels of inorganic arsenic over an extended period may produce darkening of the skin and the appearance of small "corns" or "warts" on the palms, soles, and torso. Redness and swelling can result from skin contact.

Organic arsenic compounds are less toxic than inorganic arsenic compounds. Exposure to high levels of some may cause effects similar to those seen with inorganic arsenic. Indeed, studies have shown that inorganic arsenic can increase the risk of lung, skin, bladder, liver, kidney and prostate cancer.

Chromium is a naturally occurring element found in animals, plants, rocks, soil, and volcanic dust and gases. It is present in the environment in several different forms. The most common are chromium (0), chromium (III), and chromium (VI). No taste or odour is associated with chromium compounds. Chromium (III) occurs naturally in the environment and is an essential nutrient, while chromium (VI) and chromium (0) are generally produced as by-products of industrial processing.

Chromium (III) is essential in the metabolism of sugar, protein, and fat. Breathing high levels of chromium (VI) can cause nasal irritation, including runny nose, and nosebleeds, and also ulcers and holes

in the nasal septum. Ingesting large amounts of chromium (VI) may result in stomach upsets and ulcers, convulsions, kidney and liver damage, and even death. Contact with certain chromium (VI) compounds can cause skin ulcers. Some individuals are extremely sensitive to chromium (VI) or chromium (III), with allergic reactions consisting of severe redness and swelling of the skin having been reported. It has been shown that chromium (VI) compounds can increase the risk of lung cancer and animal studies have also shown an increased cancer risk.

Regulation, Standards and Analysis

The environmental protection agencies of most governments around the world regulate the acceptable level of toxic metals in water. In the USA, for example, it is now 33 years since the publication of the first Clean Water Act. In its Drinking Water Directive, the European Union has set mandatory standards for water quality which are being transposed into each member state's legislation (figure 2). This process started in 1998, and is ongoing. For certain important metals such as lead and arsenic, standards have been tightened recently. For others, new lower targets must be achieved by 2008 or 2013. In Asia, the WHO's International Standards for Drinking Water has been adopted as the basis for many national standards or targets.

PARAMETER	VALUE	UNIT
Antimony	5.0	µg/l
Arsenic	10	µg/l
Cadmium	5.0	µg/l
Chromium	50	µg/l
Copper	2.0	mg/l
Lead	10	µg/l
Mercury	1.0	µg/l
Nickel	20	µg/l

Figure 2: Permitted levels of metals in European drinking water

A variety of analytical techniques have been used to measure heavy metal concentration at the low levels required by the standards. Simple colorimetric methods are straightforward to perform and inexpensive, but reproducibility can be poor, and for several metals, users are working at the limits of detection for the technique. At the other end of the scale, atomic absorption and X-ray fluorescence techniques can be used. However, high capital costs, a complex working methodology and extended analysis times limit its use for water analysis, especially in the field.

Anodic Stripping Voltammetry (ASV) concentrates the metal under test by plating it onto an appropriate electrode. The deposited metal is subsequently stripped off, a process which generates a current that can be measured. The current is directly proportional to the concentration of metal. In addition, the electrical potential (voltage in millivolts) at which the metal is stripped is characteristic for each metal. This means the metal can be identified as well as quantified. ASV systems offer low acquisition and maintenance costs, simplicity in use, multiple metals capability and reproducible measurements at 5ppb (or lower) detection limits.

ASV Application Note: Chromium (VI) in Water

Chromium (VI) is analysed using a bare carbon electrode. Using the PDV6000 portable analyser, the limit of detection for chromium (VI) is 5ppb. Following a simple electrode conditioning cycle, the system is 'blanked' and a standard measured. Up to 5 samples can then be analysed before recalibration is needed. The protocol is fast – deposition time for each measurement is between 60 and 150 seconds. Reproducibility at 100ppb has been shown to be better than 5%, comparable with atomic absorption and X-ray techniques.

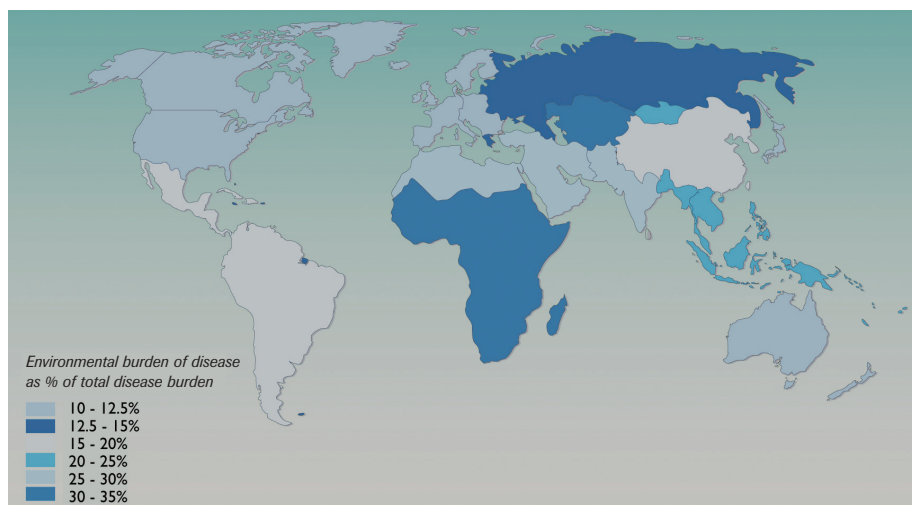


Figure 1: Estimated proportion of total disease burden caused by environmental factors, by region of the world

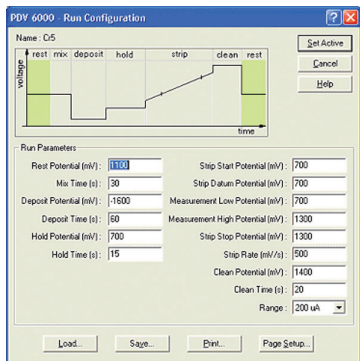


Figure 3 – Example software screen showing typical run parameters for measuring Cr (VI) with a PDV6000 portable analyser

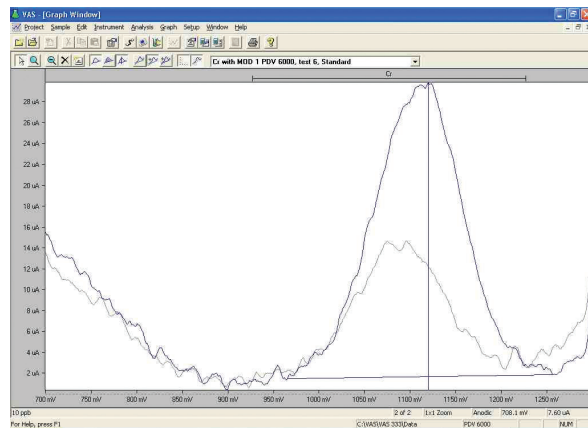


Figure 4 – 5 & 10ppb Cr (VI) in 50% Hg electrolyte, deposition time 150 seconds

Typical run parameters are shown in figure 3 above and the results for 5 and 10ppb chromium (VI) standards are shown in figure 4.

ASV Application Note: Arsenic in Water

Using river water samples, the PDV6000 portable analyser provides excellent linearity over a measurement range of 2 to 100ppb (figure 5). In this application example, reproducibility was demonstrated to be better than 5% over 5 measurements, at 50ppb. The ASV technique clearly discriminates between samples with 0, 10 & 20ppb arsenic (figure 6).

Summary

The well-established technique of ASV compares favourably to alternative analytical approaches for measuring heavy metals. Cost-effective and flexible modern systems generate consistent results in the field, in the laboratory, or on-line in a process control situation. As governments, companies and those involved in environmental monitoring focus on the effects of heavy metals and the control of levels in water, ASV looks set to support analysis activities into the future.

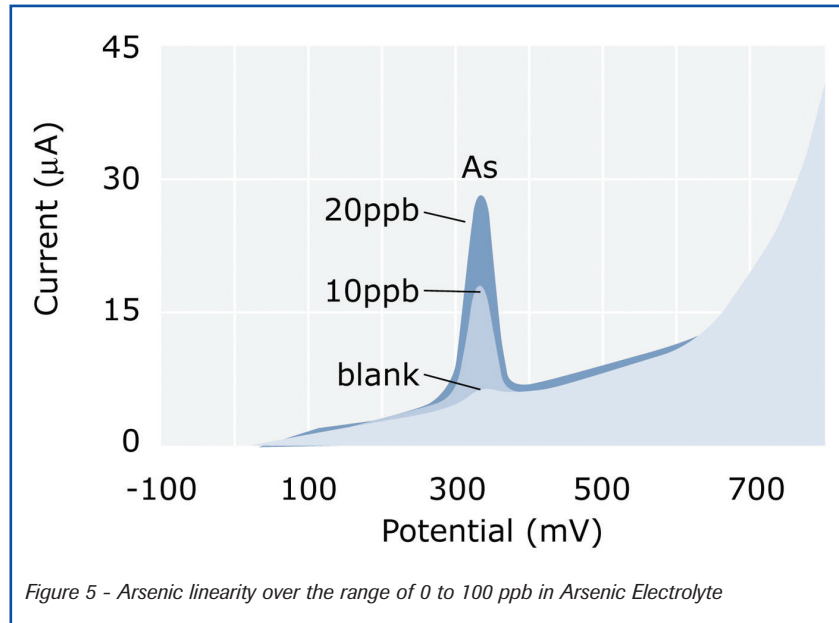


Figure 5 - Arsenic linearity over the range of 0 to 100 ppb in Arsenic Electrolyte

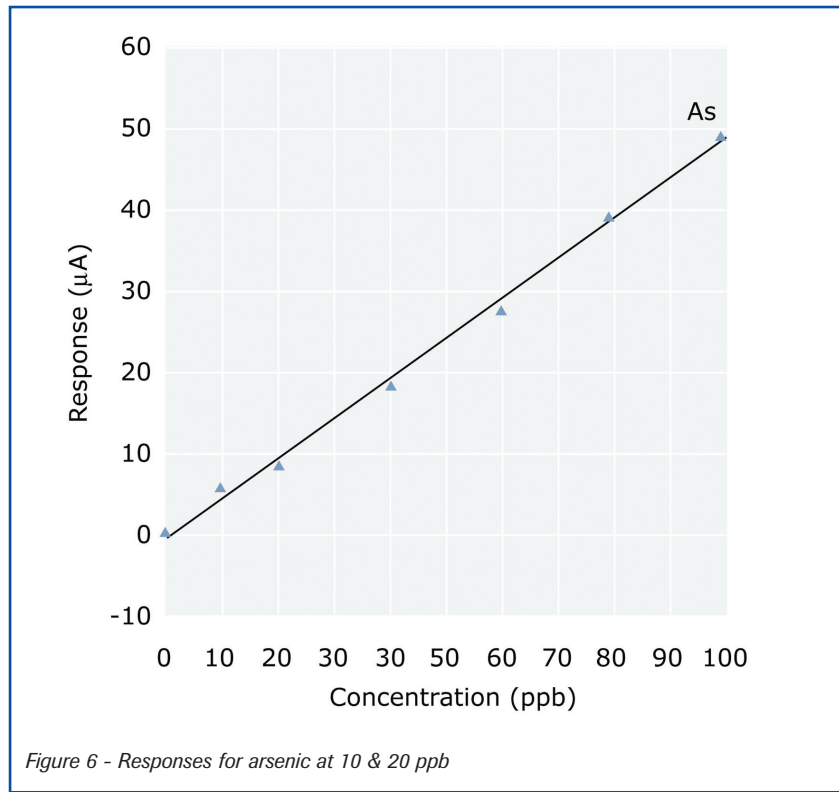


Figure 6 - Responses for arsenic at 10 & 20 ppb

Heavy Metal Analysis with MTI

All experimental data presented in this article were generated with MTI analysis systems, from Lab21. MTI systems use the well-established technique of Anodic Stripping Voltammetry (ASV) to generate accurate and reproducible results for a wide range of metals. The technique can be applied to water samples without any sample pre-treatment. Other sample types, soil for example, need to be extracted before analysis can be performed.

MTI systems are available as portable, in-field analysers, bench-top laboratory systems or fully automated on-line instruments suitable for process control. Illustrated is the OVA5000 designed for automated online, continuous monitoring.

For a detailed primer on Anodic Stripping Voltammetry, and more information about the Lab21 range of MTI analysis systems, visit www.lab-21.com

