

# Mercury Determination in Differing Environmental Sample Types via Cold Vapour Generation Atomic Absorption and Atomic Fluorescence Spectroscopy

The measurement of mercury from ultra-trace and trace concentrations up to levels considered abundant, in a gamut of environmental sample types, is essential in the generation of data for environmental monitoring. Such data can be used to establish the magnitude of release, or emission, of mercury and subsequently its spread from source into the wider physical environment - the air, waters, soils and plant life for example. Mercury is becoming more prevalent in the environment and the magnitude of its presence needs to be observed and reduced. Therefore its measurement is becoming more important.

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A number of analytical techniques are available for the measurement of mercury with varying degrees of capability as well as limitation within the spectrum of sample types. The combination of cold vapour generation and either atomic absorption spectroscopy or atomic fluorescence spectroscopy allows the measurement of mercury from sub parts-per-trillion concentrations up to levels of hundreds of parts-per-billion. Such a measurement range allows the study of mercury and its movement and/or accumulation

in environmental samples of all types as well as sample types of any other field.

It is recognised that the release and emission of mercury into the environment, and subsequently its movement and accumulation, correlates with industrialisation and population growth. Therefore, without measures to control such release and emission, an obvious conclusion may be drawn in that overall human exposure to mercury has increased and will continue to do so. Currently there is legislation and regulation in place, under the remit of such bodies as the Environmental Protection Agency (EPA) and the United States Food and Drug Administration (FDA), to limit human exposure to mercury and as part of such there are maximum allowable concentrations in foodstuffs, for example. In 2013 it is intended that a global legal instrument is to be signed and established with the aim of reducing the release and emission of mercury from, but not limited to, industrial processes (such as mining, deforestation, waste incineration and the burning of fossil fuels for example) and products that may contain mercury (such as dental amalgams, electrical applications, laboratory and medical instrumentation and batteries etc...). The key to the reduction of presence of any contaminant in the environment is the ability to perform representative and accurate measurement. In the case of mercury, for many analytical techniques, measurement can be difficult due to its physical and chemical properties. In inductively coupled plasma based instrumentation, for example, cross contamination and the occurrence of 'memory effects' are particularly problematic at the sample introduction apparatus.

Due to the nature of cold vapour generation, it is relatively straight forward to extract the analyte of interest, in this case elemental mercury,

from a sample matrix for the purpose of measurement via atomic absorption spectroscopy or atomic fluorescence spectroscopy. Such a combination of extraction and measurement allows the accurate and precise determination of mercury at concentrations as low as 0.05 parts-per-trillion (ppt - e.g. ng L<sup>-1</sup> or ng Kg<sup>-1</sup>) up to levels as high as 400 parts-per-billion (ppb - e.g. µg L<sup>-1</sup> or µg Kg<sup>-1</sup>). Such a measurement range allows the ability to study the release, or emission, of mercury and its movement and accumulation in the environment as well as movement into the food chain at different levels. In this article we highlight the advantages and some applications of cold vapour atomic absorption and atomic fluorescence spectroscopy in the field of environmental analysis and monitoring.

## Instrumentation and Principles of Operation

Cold vapour generation based atomic absorption spectroscopy (CVAAS) and atomic fluorescence spectroscopy (CVAFS) instruments, such as the CETAC Technologies Quicktrace™ M-7600 and M-8000 systems (as shown in Figures 1 and 2), operate on the principle of extracting mercury from a sample in vaporous elemental form following the reduction of inorganic mercury with a reducing agent such as stannous chloride in a gas-liquid separator (GLS). Elemental mercury vapour is carried away via a gas flow such as argon or nitrogen from the sample matrix, dried in a moisture trap or similar and detected. In the case of atomic fluorescence spectroscopy mercury may also be captured for a period of time on a gold trap prior to analysis. This has the added benefit of analyte pre-concentration which is particularly useful in samples

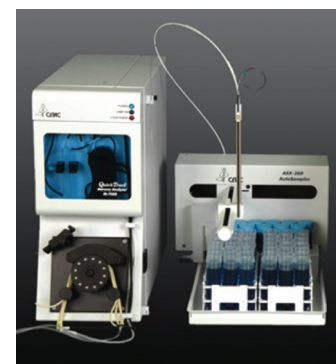


Figure 1: The CETAC Technologies Quicktrace™ M-7600 Cold Vapour Atomic Absorption Spectrometer Mercury Analyser.

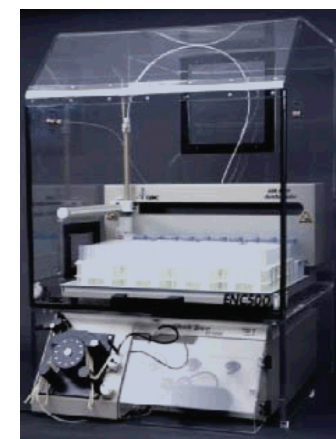


Figure 2: The CETAC Technologies Quicktrace™ Cold Vapour Atomic Fluorescence Spectrometer Mercury Analyser.



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of very low mercury concentration. Following capture the mercury can be liberated for detection via heating in an automated furnace.

## Sample Preparation

For both CVAAS and CVAFS sample preparation is straight forward, the aim of which is to produce a representative and homogenous sample from which elemental mercury may be liberated in vapour form via reduction. A typical approach to sample preparation is digestion and oxidation followed by a reduction step with the appropriate agents and dilution in preparation for measurement. Some samples, solids for example, may require prior breakdown via strong acid conditions and heating. For each analysis a series of matrix matched blanks and standards are also prepared.

## Results and Discussion

We present the data generated from the measurement of three types of environmental sample using CVAAS and CVAFS.

### Seawater

Samples of the certified reference material (CRM) Coastal Seawater BCR-579 were digested and oxidised via exposure to 0.1 N potassium bromide/potassium bromate solution followed by reduction with hydroxylamine (12 %). Digested samples were subsequently stored in hydrochloric acid. During analysis the inorganic mercury of the sample was reduced to elemental

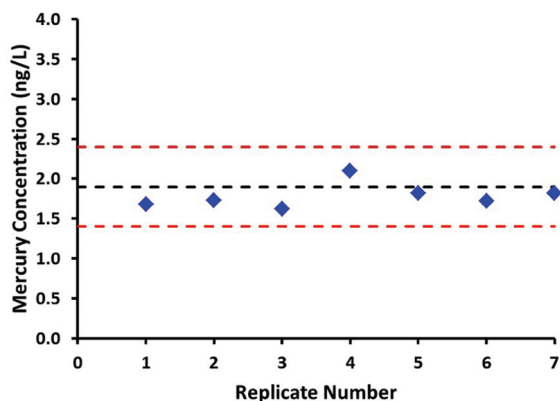


Figure 3: A graph comparing the measured mercury concentration of the Coastal Seawater BCR-579 CRM across the seven replicate analyses. The seven measurements all fall very close to the 1.9 ng L<sup>-1</sup> target concentration of this CRM (which is represented in this graph along the black dashed line) and within the target tolerance of  $\pm 0.5$  ng L<sup>-1</sup> (which is indicated by the two red dashed lines).

mercury for measurement following exposure to stannous chloride (10 %) in hydrochloric acid (7 %). The CRM seawater was then analysed in conjunction with matrix matched blanks and standards. The data generated from the analysis of the seawater (n = 7) is shown in Figure 3. The mean measured concentration of mercury in BCR-579 was 1.78 ng L<sup>-1</sup> (% RSD = 8.8 %) which has good agreement with the target concentration of this CRM of 1.9 ng L<sup>-1</sup>  $\pm 0.5$ .

### Water

Samples of CRM National Institute of Standards and Technology (NIST) Water 1641c were digested and oxidised in the same manner as the CRM seawater as described above followed by the same reduction approach. Samples were similarly stored in hydrochloric acid and analysed in conjunction with matrix matched blanks and standards. The data generated from the analysis of the water samples (n = 7) is shown in Figure 4. The mean measured concentration of mercury in Water 1641c was 1.49 mg L<sup>-1</sup> (% RSD = 1.2 %) which shows good agreement with the target concentration of 1.47 mg L<sup>-1</sup>  $\pm 0.04$ .

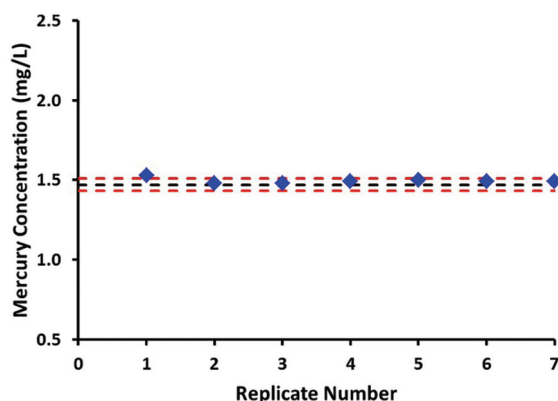


Figure 4: A graph comparing the measured concentration of the NIST Water 1641c CRM across the seven replicate analyses. The seven measurements all fall very close to the 1.47 mg L<sup>-1</sup> target concentration of this CRM (which is represented in this graph by the black dashed line) and within the target tolerance of  $\pm 0.04$  mg L<sup>-1</sup> (which is indicated by the two red dashed lines).

### Soil

Samples of CRM NIST 2710 Montana Soil were digested in aqua regia under heat and subsequently oxidised with potassium

permanganate. The potassium permanganate of the resulting digest solution was reduced by the addition of hydroxylamine. The resulting solution was then in a position to be analysed, during which inorganic mercury was reduced to elemental mercury via the online addition of stannous chloride (10 %) in hydrochloric acid (7 %). As with the seawater and water analysis described above the CRM soil samples were analysed in conjunction with matrix matched blanks and standards. The data generated from this soil analysis (n = 7) is shown in Figure 5. The mean measured concentration of mercury in this CRM soil was 32.28 mg Kg<sup>-1</sup> (% RSD = 3.88 %) and similarly showed good agreement with the target concentration of 32.6 mg Kg<sup>-1</sup>  $\pm 1.8$ .

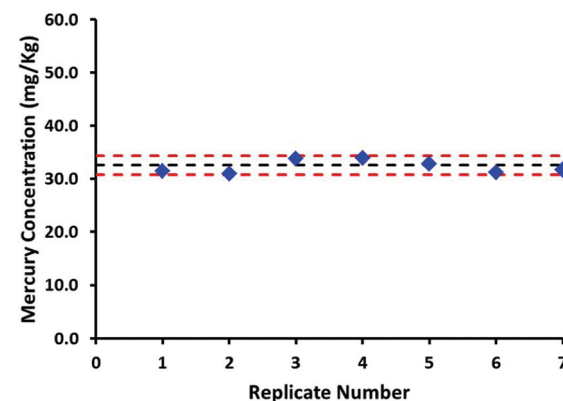


Figure 5: A graph comparing the measured concentration of NIST 2710 Montana Soil CRM across the seven replicate analyses. The seven measurements all fall very close to the 32.6 mg Kg<sup>-1</sup> target concentration of this CRM (which is represented in this graph along the black dashed line) and within the target tolerance of  $\pm 1.8$  mg Kg<sup>-1</sup> which is indicated by the two red dashed lines).

## Conclusions

CVAAS and CVAFS provide the analyst with a means of very accurate and precise measurement of mercury from ultra-trace to levels considered abundant in environmental sample types. This ability is considerably beneficial to analytical laboratories and in the monitoring of environmental samples. Considering the toxicity of mercury and its movement throughout the environment the ability to measure ultra-trace levels is just as important as measuring levels that are much higher. CVAAS and CVAFS are therefore ideal tools for environmental monitoring particularly with the preparation of the global legal instrument in mind and the emphasis that this will put on the measurement of mercury in environmental samples and across the wider scientific disciplines.