

FACT SHEET



Cyanide: groundwater sampling / analysis

introduction

Correct sampling, transportation and analysis of water samples for cyanide species is more difficult than for most chemical analysis.

This arises from the ability of cyanides to participate in a variety of chemical and microbiological reactions, and is further complicated by the variety of cyanide species typically found in water samples.

Whilst problems can arise with any cyanide sample, they most commonly manifest in samples from groundwater monitoring bores, results for which are compared to environmental criteria.

recommended sampling method

The recommended methodology for sampling is to filter the sample on site, prior to adding caustic, to remove sediment from the sample.

The filtered sample is then immediately placed in a non-transparent (generally black plastic) bottle with sufficient caustic to give a pH of at least 12. The sample should be kept cold and transported to the lab as soon as possible, preferably the day of sample collection.

Since cyanide samples decompose even after preservation, the Australian standard holding time between sampling and analysis is 24 hours. In the laboratory, for both WAD and Total Cyanide analysis, the received sample should be shaken thoroughly and an aliquot containing a mixture of liquid and the precipitated hydroxides should be analysed.

AS 5667 and the International Cyanide Management Code outline the preferred method for analysis of WAD and Total Cyanide by manual distillation (eg as per methods 4500—CN in APHA 20th Ed).

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field filtering: the importance

Water samples pumped directly from bores will almost always contain some sediment. If the bore in question also contains cyanide species then that sediment (soil material) will have cyanide species adsorbed onto it (i.e. in a non-mobile form).

For groundwater monitoring purposes the cyanide of interest is the amount which is dissolved in the water and therefore moving through the aquifer. If the soil/sediments are not removed by field filtration and the sample is analysed using the correct method (shaken before sub-sampling), they will produce a higher than true result on analysis and cause guideline values to be exceeded.

It is important though to perform this filtration as quickly as possible (ideally using pressure filtration) to prevent the loss of any free hydrogen cyanide from the sample before placing into the preserved bottle. Hydrogen cyanide is a volatile gas and can be lost easily if there is a significant delay between sampling and the preservation with caustic.

If the sample is not field filtered, prior to preservation, the sample received at the laboratory may not be representative of the groundwater being sampled.

laboratory sub-sampling

The preservation with caustic to pH 12 or above is required to prevent loss of any cyanide as hydrogen cyanide gas during transport. Changing the pH of the groundwater sample to pH 12 also has the effect of causing the precipitation of metals in the water as a white solid that settles to the bottom of the bottle.

This white precipitate is mostly carbonates and hydroxides of magnesium and other metals found in all ground waters. Unfortunately, these precipitates also take with them many cyanide species originally present in the bore water as they become part of or are chemically bound to the hydroxide precipitate. This process is known as co-precipitation.

When the sample arrives in the laboratory a sub-sample is taken for analysis. Since many cyanide species originally in the water are now stuck to the white precipitate at the bottom of the bottle on arrival, to get a true result the lab must shake the sample thoroughly before sub-sampling for analysis.

Failure to shake or filter the preserved sample before sub-sampling may give results that are artificially low in cyanide.

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Thus, the preferred method is to take a sub-sample, after vigorous shaking, that contains an evenly distributed amount of suspended precipitate with cyanide bound to it as was present in the original sample (a total sub-sample).

If conventional distillation methods are used the precipitate presents no problem. However, if automated flow-injection is used then the presence of precipitates and sediment can lead to fouling of the flow paths and failure of the instrument.

Because blockage problems occur, flow injection analysis samples are usually filtered or allowed to settle before being decanted from the top of the bottle. As stated this leads to an artificially low result for real world samples which have formed co-precipitates.

This absolute need to shake the sample before sub-sampling for analysis, also results in stirring up any mud/soil/sediment (and its bound cyanide) in the bottle. This may cause artificially high results and again highlights the need for field filtering prior to preservation.

thiocyanates

Thiocyanate (SCN) is formed in groundwaters, tailings dams or process waters where cyanide is present along with sulphides.

The reaction is an equilibrium (reversible) reaction, and the formation of thiocyanate is favoured by high pH (as found when in a preserved cyanide sample).

Sulphides can also be removed whilst field filtering, by the addition of a small quantity of lead carbonate. The preferred, traditional cyanide analysis methods based on distillation do not include thiocyanate as a cyanide species. However, flow injection analysis methods do not distinguish between thiocyanate and other cyanide species.

If the sample contains high levels of thiocyanate, then flow injection analysis will give higher cyanide readings than conventional methods. Previous test work by MPL showed that thiocyanate increases the apparent cyanide level in samples by 41 mg/L for every 100 mg/L of thiocyanate.

As outlined in the International Cyanide Management Code, when flow injection is used, a separate analysis should be performed for thiocyanate and the measured cyanide levels reduced accordingly (by 0.41 mg/L for every 1 mg/L of thiocyanate based on MPL results).

We note here that some WA mine waters contain very high levels of thiocyanate, in the order of 100 mg/L.

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