



guardians of drinking water quality
DRINKING WATER INSPECTORATE

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SAMPLE PRESERVATION AND
PREPARATION FOR METALS

ANALYSIS OF DRINKING WATER

DWI GUIDANCE ON SAMPLE PRESERVATION AND PREPARATION FOR METALS ANALYSIS OF DRINKING WATER

Purpose

Regulation 16(2)(c) requires companies to ensure that samples are kept at such temperature and in such conditions as will secure that there is no material alteration in the concentration or value for the measurement or observation of which the sample is intended. This is relevant to a number of parameters.

In order to fulfil the requirements of the above regulation in respect of metal determinands, the sample needs to be preserved at the time of sampling or as soon as it enters the laboratory. Further pre-treatment may then be necessary to ensure that all the metal of interest present in the sample is in the form and state required for analysis. In practice this usually means that any of the metal of interest present in particulate form, or adsorbed onto particles in the sample or the surface of the sample container, is taken into solution. The exception to this is antimony where the oxidation state may also be of prime importance.

In practice, sample preservation and pre-treatment for metal determinands are interlinked and must be considered together. Some laboratories assume that the preservation stage is adequate to dissolve any particulate material present, as long as there is a suitable time lapse between sampling and analysis. Other laboratories have adopted a practice of only subjecting samples to a rigorous pre-treatment if particulate material can be seen in the sample or the sample has an elevated turbidity. These practices have been shown to be unreliable and should not be used for regulatory analysis.

Best Practice for sample preservation

Best practice for sample preservation is documented in ISO 5667 Part 3:2003.

The recommendations on best practice for pre-cleaning sample containers is given in paragraph 3.2.2.4. Acid-washed plastic or borosilicate glass containers may be used, except for mercury, for which acid-washed borosilicate glass containers must be used.

For most metals the recommended preservation is acidification to pH1 to 2 with concentrated nitric acid. The exceptions are mercury which additionally requires the addition of potassium dichromate, and antimony, for which hydrochloric acid should be used if analysis is to be by hydride generation.

Best practice for sample pre-treatment

Best practice for sample pre-treatment for metal determinands is documented in ISO 15587 Parts 1 and 2. These recommend digestion by boiling with aqua regia or nitric acid. The nitric acid method is not suitable for antimony when it is determined by hydride generation. Procedures are described using both open and closed systems, with digestion using standard heating devices and microwave digestion.

Certain analytical procedures may specify alternative preservation and pre-treatment regimes. It is acceptable to use these methods, provided they are properly documented and published by an authoritative source of analytical methods. They also need to be validated as part of the overall method. Where the method is dependent on specific preservation and pre-treatment regimes these should always be used (this advice is contained within the ISO Standards) (eg some methods for mercury analysis).

Analytical blanks

Analytical blanks should always be subject to preservation and pre-treatment regimes identical to regimes applied to samples. They should be processed with the batch of samples to which they relate using the same bottle/batch of each reagent. If blank correction is applied, it should be these blanks which are used to correct all samples in the batch.

When carrying out trace analysis, contamination of reagents and standards is a significant source of error and should be minimised by only using the grade of reagent or standard appropriate to the method being used. Standards and reagents suitable for AAS have been found to be unsuitable for ICP-MS work.

It may be necessary to also run reagent blanks, prepared in the same way as standards, for blank correction of standards.

Regulatory Requirement

The Inspectorate expects laboratories to follow best practice in order to meet the requirements of regulations 16(2)(c) and 16(5)(b), unless an alternative method can be shown to be equally satisfactory. Real samples and, if necessary, spiked real samples containing concentrations of each metal of interest at concentrations close to the PCV including natural particulate material should be used for testing. For lead analysis this includes particles of metallic lead, and naturally occurring particles of oxides, hydroxides or salts of all metals. The principles of testing and calculation of results given in the accompanying guidance on stability trials should be followed.

Alternative Preservation and Pre-treatment Regimes

Samples for mercury should always be preserved at the time of sampling because of the highly volatile and highly reactive nature of the determinand.

The ISO method recommends preservation of the sample at the time of sampling. If this is adopted, then a representative aliquot may be taken from the sample for pre-treatment prior to analysis.

The Inspectorate accepts that some companies prefer not to use bottles with acid preservative for samples taken at consumers' taps, with the exception of mercury. This is on health and safety grounds. In such circumstances the samples should be preserved immediately on arrival at the laboratory. However the whole sample container should then be subject to an additional pre-treatment step before any sample is withdrawn. This is to take account of any metals that have adsorbed onto the surface of the container and should be applied for both plastic and glass sample containers.

The additional pre-treatment step may be to heat the acidified sample container in an oven at 80°C for 12 hours (in practice over night) before cooling the contents and sub-sampling for analysis. At least one laboratory has shown this to be satisfactory and comparable with preservation at the time of sampling. This procedure can also be used with samples preserved at the time of sampling. In either case a further digestion step may be required prior to analysis, especially for lead analysis.

Laboratories may wish to establish which combination of procedures is most appropriate for their sample matrices.