



Heavy metals analysis

Correct measurement results are a prerequisite for compliance with limit values, which are always specified as **total metals**. Heavy metals such as copper, nickel, zinc, etc. can be quickly and reliably determined in aqueous samples with the help of the Hach® LCK cuvette tests. **Matrix factors** (e.g. interference ions, colour, turbidities, etc.) may have a negative impact on the measurement and cause false results to be obtained. If the sample preparation is inadequate, frequently used **complexing agents** such as EDTA, NTA and citric acid may also cause low-bias results to be obtained, as they bind the metal ions and thus inhibit the detection reaction. In practice it is necessary to carry out a **sample digestion** before the metals are analysed.

Essential sample preparation

Sample preparation is essential before an analysis of the **total metal content** is carried out. This is because the composition of the wastewater from individual technical processes is often unknown. Hidden complexing agents may be introduced by bath additives, e.g. in electrolytes, degreasing baths and cleaning baths, so that the sample may have to be digested before it can be analysed.

Similar considerations apply to turbid water. The total metal content cannot be correctly determined unless the sample is homogenised (to ensure that the suspended solids are evenly distributed) before it is digested. Under no circumstances should the sample be filtered, as this would remove all the metals attached to the solids. The analysis result would then be too low.

The situation is different when **dissolved metals** have to be determined. In this case, clear samples can be analysed immediately using the appropriate cuvette test, while samples that contain turbidities or suspended solids can be filtered using membrane filtration set LCW904 (1.2 µm) or LCW916 (0.45 µm) before the analysis.

Homogenisation

Turbid samples must be homogenised prior to the digestion step, to ensure that the contents are evenly distributed before sampling. According to DIN 38402-A30 – July 1998, the frequency of the magnetic stirrer must be set so that the depth of the surface vortex is about 10% of the height of the liquid. The appropriate sample volume must then be pipetted off while stirring continues.

Setting the pH

The pH setting before and after the digestion is especially important for precise metal analysis. The necessary pH of less than 1 before the digestion



LCW902 Crack Set with acid, oxidising agent and buffer solution.

is obtained by adding the sulphuric acid provided in the Crack Set. If, in exceptional cases, the correct value is not reached (e.g. when the sample has a high buffering capacity), additional sulphuric acid must be added.

After the digestion the pH must be checked to ensure that no hydroxide is precipitated. Ideally the pH should be in the range between 2.5 and 5, and this is usually the case after the addition of the buffer solution from the Crack Set. If it is not, more sulphuric acid or more buffer solution can be added (both are contained in the Crack Set) until the correct pH is obtained.

Sample digestion with the LCW902 Crack Set

The Crack Set is suitable for the digestion of the metals lead, cadmium, iron, copper, nickel and zinc. Undissolved and complexed heavy metals are dissolved by heating in an acid environment in the presence of an oxidising agent (either 1 hour at 100 °C in a LT200 thermostat or 15 minutes in a HT200S high temperature thermostat). A comparison of the results obtained before and after the digestion shows whether the digestion is necessary. If the digested sample gives higher measured values, bonded metals are present in the undigested sample, which are not accessible for analysis before the digestion is carried out. In this case, a sample preparation with the Crack Set is essential before the total metals are determined.

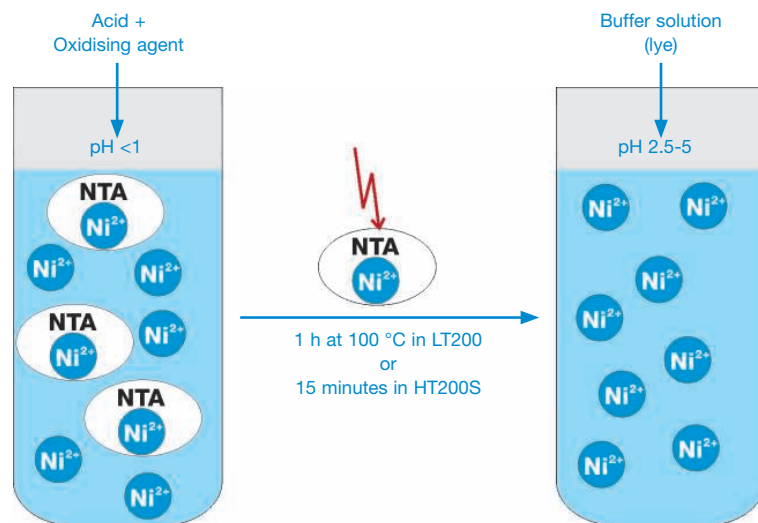


Fig. 1: Action of the Crack Set: During the digestion, the acid and the oxidising agent dissolve the metal ions out of the complexes.

Action of the Crack Set

Figure 1 shows how the Crack Set acts on a water sample. In this example, complex nickel compounds are oxidatively digested by heating in an acid environment.

The complexing agents are broken down under the reaction conditions and the heavy metal ions (in this case nickel) enter into solution. This also usually eliminates colourations and turbidities (metal hydroxides and carbonates, and metals attached to solids).

The sample preparation with the LCW902 Crack Set can usually be carried out as described in the working procedure. In special cases, however, the procedure may have to be amended to suit the sample and its matrix (e.g. heavily polluted samples or samples with a high buffering capacity).

Improved digestion capacity: double digestion

If reducing agents, organic components or a high proportion of metal complexes are present, the amount of oxidising agent may be insufficient to completely digest the sample.

Simply diluting the sample reduces interference factors in the matrix, while increasing the digestion capacity. Increasing the amount of oxidising agent improves the digestion capacity.

This variant is especially suitable for low concentration of heavy metals, e.g. if further dilution would reduce the concentration below the lower limit of the measuring range.

Double digestion procedure

Allow the reaction tube to cool slightly after the first digestion period of 60 minutes in the LT200 or 15 minutes in the HT200S, then add the additional oxidising agent (another 2 mini-spoonfuls from the Crack Set). Heat again for 60 or 15 minutes in the thermostat. Adding the oxidising agent in two steps ensures that additional oxidising agent is available in the sample solution after the first digestion.

Other sample digestions

A digestion is integrated in the package of the cuvette test LCK313 for the determination of total chromium. Only if the samples are heavily polluted or contain a high proportion of reducing agents, or are still turbid after the digestion should the determination be carried out according to a special analysis procedure (LYW513).

A sample digestion is also carried out for the analysis of total silver (LCW954).

Accurate results thanks to plausibility checks

Information about the interference factors in the matrix of the sample is especially important for the analysis of heavy metals. Diluting the sample often proves to be a simple method of eliminating interferences. Preliminary tests should therefore be carried out to clarify whether, and in what ratio, the sample should be diluted, and to determine the most suitable digestion variant.

Dilution

To carry out a plausibility check by means of dilution, the sample is diluted with distilled or deionised water before the digestion is carried out. At least two digestions should be carried out with the Crack Set at different dilution levels, e.g. 1:5 (2 mL sample + 8 mL dist. water) and 1:10 (1 mL sample + 9 mL dist. water) and the subsequent determina-

tion should yield a matching (plausible) result. Naturally the results must be within the given measuring range. At low metal concentrations, spiking the sample is a better alternative.

Spiking

This means adding a known concentration of the analysis parameter to the sample before the digestion is carried out (Addista spiking solution) and then evaluating the spiked solution using the appropriate cuvette test (E1). At the same time a non-spiked sample is measured (E2). The spiking amount is then calculated: $A = E1 - E2/2$. If the spiking amount is within the given confidence interval (see back of Addista package), the sample contains no interference substances and can be analysed without diluting it any further.

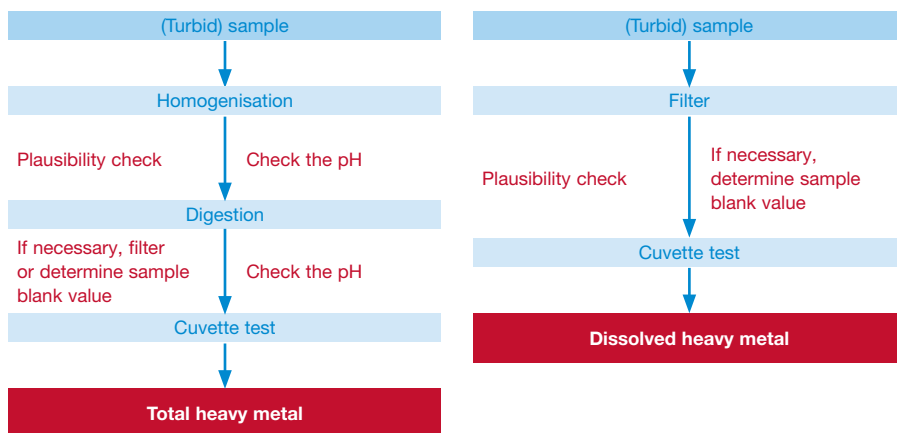


Fig. 2: Work steps for determining the total heavy metal content and the dissolved heavy metal content.

Practical tips

- If samples have a high buffer capacity, acid and buffer solution may have to be added in quantities that differ from the working procedure (see Setting the pH).
- Turbidities in the digested sample can be filtered off (membrane filtration set LCW904 or LCW916).
- Colourations in the digested sample must be taken into account by determining a sample blank value (see Hach Application "Sample-specific blank value", DOC042.52.00280).
- If a sample is heavily polluted, it is possible that the metal compounds are not all sufficiently digested. In this case a double digestion should be carried out (see Improved digestion capacity).
- If a sample contains a high concentration of salts or a high organic load, rapid cooling of the reaction tube after the digestion favours the formation of small crystals and prevents the formation of voluminous precipitates, which would encapsulate the metal ions that are to be analysed. At the end of the digestion the sample should be left to cool for 5–10 minutes, before being neutralised and then cooled under cold water (caution: wear protective clothing!) or in a refrigerator. The supernatant liquid can then be decanted or pipetted to separate it from the precipitates.
- Contaminated reaction tubes can easily cause high-bias results to be obtained. Especially in the trace range, a clean digestion vessel is a prerequisite for correct analysis results! Clean with a bottle brush and follow by repeated rinsing with distilled water. Badly contaminated vessels should not be used again!
- Wastewater treatment with milk or lime increases the concentration of calcium in the water. This interferes with the photometric determination of nickel (turbidity), chromium(VI) (also turbidity) and cadmium (undesirable colour reaction). In this case, either the LCW903 calcium separation set (Cr, Cd) or Application A128 (Ni) should be used. The latter describes how the addition of citrate can prevent undesirable turbidity when nickel is being determined.



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Literature

Working procedures for the Crack Set and the cuvette tests for lead, cadmium, chromium, iron, copper, nickel, silver, zinc, tin

Overview "Operational analysis in the metal industry", Art. no. DOC062.52.00273