



Sodium Chloride - Analytical Standard



Determination of Copper Zinc Dibenzylidithiocarbamate Photometric Method

EuSalt/AS 005-2005

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1. SCOPE AND FIELD OF APPLICATION

The present EuSalt Analytical Standard describes a photometric method using zinc dibenzylthiocarbamate for the determination of copper in sodium chloride. The method is applicable to products of copper content (Cu) equal to or greater than 0.01 mg per kilogram of salt.

2. PRINCIPLE

Dissolution of the sample in hydrochloric acid.

Extraction of the coloured complex formed by reaction of the copper with zinc dibenzylthiocarbamate into carbon tetrachloride. Photometric measurement of the organic extract at a wavelength of approximately 435 nm.

The determination is selective in an acidic medium, which suppresses interferences, especially of iron, manganese, nickel and cobalt.

3. REAGENTS

Unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

3.1. Carbon tetrachloride, redistilled, (see 8.5.)

3.2. Hydrochloric acid, $c_{(\text{HCl})} \approx 2 \text{ mol/l}$

3.3. Zinc dibenzylthiocarbamate,

0.5 g/l solution in carbon tetrachloride (3.1.)

3.4. Copper, stock solution I, $\beta_{(\text{Cu})} = 1000 \text{ mg/l}$,

commercial standard solution or to be prepared as follows. Dissolve 1.000 g of copper (metal 99.9%) in a mixture of 20 ml of nitric acid [$\rho \approx 1.40 \text{ g/ml}$, 65% (m/m) solution] and 60 ml of water. Make up to 1000 ml in a one-mark volumetric flask and mix.

3.5. Copper, stock solution II, $\beta_{(\text{Cu})} = 1 \text{ mg/l}$

Transfer 1.00 ml of copper stock solution I (3.4.) into a 1000 ml one-mark volumetric flask, make up to the mark and mix.

Prepare this solution immediately before use.

4. APPARATUS

Usual laboratory equipment (see 8.3.) and:

4.1. Spectrophotometer or

4.2. Photocolorimeter fitted with a filter ensuring maximum transmission between 430 and 440 nm.

Note: Specify the type of apparatus used (spectrophotometer or photocolorimeter), the path length and the wavelength (or type of filter).

5. SAMPLING AND SAMPLES (see 8.2.)

A test sample of 500 g should be taken for analysis, ensuring it is representative of the whole batch.

6. PROCEDURE (see 8.2.)

6.1. Test portion

Weigh, to the nearest 0.1 g, about 100 g of the test sample.

6.2. Test solution

Transfer the test portion (6.1.), 350 ml of water and 50 ml of hydrochloric acid (3.2.) into a 600 ml beaker. Heat to boiling until dissolution is completed.

After cooling, transfer quantitatively into a 500 ml volumetric flask, make up to volume and mix.

Note: If the test solution is cloudy, it must be filtered prior to collection in the 500 ml volumetric flask.

6.3. Blank solution

Solution containing 100 ml of hydrochloric acid (3.2.) per litre.

6.4. Calibration

6.4.1. Calibration solutions

These preparations are used for photometric measurement in cuvettes of 4 or 5 cm optical path length.

Transfer 25 ml of hydrochloric acid (3.2.) and the volumes of copper stock solution II (3.5.) indicated in the following table into a series of five 500 ml separatory funnels, dilute to about 250 ml with water and mix.

Calibration solution No.	Copper, stock solution II, ml	Corresponding mass of copper, µg
1(*)	0	0
2	2.5	2.5
3	5.0	5.0
4	7.5	7.5
5	10.0	10.0
(*) zero calibration solution		

Note: If required the calibration can be extended. The curve is linear up to at least 50 µg of Cu.

6.4.2. Complexation and extraction

Proceed as follows with each of the five separating funnels:

- add 25.0 ml of zinc dibenzylthiocarbamate solution (3.3.) and shake well for one minute,
- after separation of the layers, run out the lower organic layer and filter it through a hydrophobic paper into a cuvette.

6.4.3. Photometric measurements

Adjust the apparatus to zero absorbance with carbon tetrachloride (3.1.).

To avoid any evaporation of the organic solvent, carry out the photometric measurements immediately using a spectrophotometer (4.1.) set up at the maximum of absorption (wavelength around 435 nm) or a photocolimeter (4.2.) fitted with the appropriate filter.

6.4.4. Calibration curve

Subtract the absorbance of the zero calibration solution from that of each of the other calibration solutions and plot a graph showing the quantities of copper (Cu), in micrograms, contained in the calibration solutions on the abscissa and the corresponding corrected absorbances on the ordinate.

6.5. Determination

6.5.1. Complexation and extraction

Transfer 250 ml (see 8.1.) of test solution (6.2.) or of blank solution (6.3.) into a 500 ml separating funnel and continue as described in paragraph (6.4.2.).

6.5.2. Photometric measurements

Carry out the photometric measurements of the two solutions obtained in (6.5.1.) according to the instructions given in paragraph (6.4.3.).

7. EXPRESSION OF RESULTS

7.1. Method of calculation

The copper content of the sample, $\omega_{(Cu)}$, is given by the formula:

$$\omega_{(Cu)} = \frac{m_1 - m_0}{m} \times \frac{V_1}{V_2}$$

where

- $\omega_{(Cu)}$ is the copper content, in milligrams per kilogram of salt
- m is the mass, in grams, of the test portion (6.1.),
- m_1 is the mass of copper, in micrograms, analysed in the final solution prepared in (6.5.1.) for the test solution (6.2.),
- m_0 is the mass of copper, in micrograms, analysed in the final solution prepared in (6.5.1.) for the blank solution (6.3.),
- V_1 is the volume, in millilitres, of test solution prepared in (6.2.),
- V_2 is the volume, in millilitres, of test solution used in (6.5.1.).

7.2. Repeatability and reproducibility

Analyses, carried out on four samples by several laboratories, have given the following statistical results, each laboratory having furnished results obtained by the same operator performing two analyses per sample:

	Rock salt	Vacuum salt	Sea salt (solid)	Sea salt (solution)
Number of laboratories	11	13	13	13
Results, mg Cu/kg salt				
Mean	0.020	0.030	0.054	0.041
Standard deviation for				
- repeatability (s_r)	0.0018	0.0030	0.0083	0.0031
- reproducibility (s_R)	0.0153	0.0159	0.0258	0.0178

The sea salt solution is the same as the solid sea salt sample, having been prepared in the same way as the test solution (6.2.).

8. REMARKS

8.1. For copper contents greater than 1 mg per kilogram of salt, the volume of test solution (6.2.) transferred into the separating funnel (see 6.5.1.) is reduced to such an extent that the amount of copper present in the final solution lies within the range of table 6.4.1. The volume of blank (6.3.) solution to use has to be reduced in the same way. The formula for calculation 7.1. must be modified accordingly.

8.2. Ensure that no trace of copper is introduced during the sampling operations, e.g. by the apparatus, and during the analysis.

8.3. All new glassware used for this determination should be washed as follows and well rinsed with water after each operation:

- with a brush and detergent if the walls are greasy,
- with diluted nitric acid, $c_{(HNO_3)} \approx 7 \text{ mol/l}$.

Use the washed glassware a few times before carrying out an actual determination. Afterwards, keep it exclusively for this determination.

8.4. The calibration curve should be repeated for each new colorimetric reagent solution (3.3.).

8.5. The use of carbon tetrachloride is restricted under the Montreal Protocol because it is an ozone depleting substance