



## Sodium Chloride - Analytical Standard



### Determination of Water-Soluble Hexacyanoferrate (II) Prussian Blue Photometric Method

EuSalt/AS 004-2015

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004-2008

## 1. SCOPE AND FIELD OF APPLICATION

The present EuSalt Analytical standard describes a photometric method for the determination of water-soluble hexacyanoferrate in sodium chloride. The method is applicable to products of hexacyanoferrate (II) content, expressed as  $K_4Fe(CN)_6$ :

- > 2.5 mg per kilogram of salt when using the direct method,
- > 0.25 mg per kilogram of salt when using the filtration method.

## 2. PRINCIPLE

Ferrocyanides [Hexacyanoferrate (II)] and iron (II) form in acid solution, the iron (II) hexacyanoferrate (II) complex. In the presence of iron (III) it oxidises immediately to Prussian Blue,  $Fe_4[Fe(CN)_6]_3$ . The absorbance of this insoluble complex is measured at a wavelength of around 700 nm.

The Prussian Blue can be filtered on a membrane filter. After re-dissolution with potassium hydroxide, the Prussian Blue is reformed in a greatly reduced volume.

## 3. REAGENTS

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

### 3.1. Sodium chloride, hexacyanoferrate-free

### 3.2. Sulphuric acid, $c_{(H_2SO_4)} \approx 0.5$ mol/l

### 3.3. Potassium hydroxide solution, $c_{(KOH)} \approx 0.05$ mol/l

### 3.4. Fe(II) / Fe(III)-solution

Add 200 g of ammonium iron (II) sulphate,  $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$ , and 25 g of ammonium iron (III) sulphate,  $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$ , into a 1000 ml volumetric flask. Dissolve with water, add 100 ml of sulphuric acid solution (3.2.), dilute to the mark and mix.

Filter the solution and store in a dark bottle.

### 3.5. Potassium hexacyanoferrate (II) stock solution I,

$$\beta_{K_4Fe(CN)_6 \cdot 3H_2O} = 1.000 \text{ g/l}$$

Transfer 1.000 g of potassium hexacyanoferrate (II),  $K_4Fe(CN)_6 \cdot 3H_2O$  into a 1000 ml volumetric flask. Dissolve in water, add 5 ml of potassium hydroxide solution (3.3.), dilute to the mark and mix.

Store in a dark bottle for a maximum of one month.

### 3.6. Potassium hexacyanoferrate (II) stock solution II,

$$\beta_{K_4Fe(CN)_6 \cdot 3H_2O} = 50.0 \text{ mg/l}$$

Transfer 50.0 ml of the stock solution (I) (3.5.) and 5 ml of potassium hydroxide solution (3.3.) into a 1000 ml volumetric flask. Dilute to the mark and mix.

Prepare this solution just before use.

## 4. APPARATUS

Usual laboratory equipment and:

### 4.1. Spectrophotometer or

### 4.2. Photocolorimeter fitted with a filter ensuring maximum transmission between 690 and 710 nm.

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

### 4.3. Membrane filter about 50 mm diameter, 0.3 $\mu$ m maximum porosity

## 5. SAMPLING AND SAMPLES

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

## 6. PROCEDURE

### 6.1. Test portion

Weigh, to the nearest 0.1 g, a maximum of 100 g (=  $m$  g) of the test sample.

## 6.2. Test solution

Transfer the  $m$  g of test portion (6.1.) and water into a 500 ml volumetric flask. Dilute to the mark and mix.

## 6.3. Blank test solution

Solution containing  $m$  g of sodium chloride (3.1.) per 500 ml.

## 6.4. Calibration

### 6.4.1. Calibration solutions

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

Transfer  $m/10$  g of sodium chloride (3.1.) and the volumes of stock solution II (3.6.) indicated in the next table into a series of five 100 ml volumetric flasks. Dilute to about 50 ml with water and add 10 ml of potassium hydroxide solution (3.3.).

Calibration solution No.	Stock solution II (3.6.) ml	Corresponding mass of $K_4Fe(CN)_6 \cdot 3H_2O$ $\mu g$
1 (*)	0	0
2	2	100
3	5	250
4	10	500
5	15	750
(*) zero calibration solution		

### 6.4.2. Colour development

Add to each flask, mixing after each addition, 5 ml of sulphuric acid (3.2.) and 5 ml of Fe(II) / Fe(III)-solution (3.4.). Dilute to the mark, mix and allow standing for 15 minutes.

## 6.4.3. Photometric measurements

Adjust the apparatus to zero absorbance against water.

Carry out the photometric measurements using a spectrophotometer (4.1.) set up at the maximum of absorption (wavelength around 700 nm) or a photocolorimeter (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 potassium ferrocyanide, in micrograms, on the abscissa and the corresponding absorbances on the ordinate.

## 6.5. Determination

### 6.5.1. Direct method

Transfer 50.0 ml of the test solution (6.2.) or of the blank solution (6.3.) into a 100 ml volumetric flask. Add 10 ml of potassium hydroxide solution (3.3.). Stir for 1 minute and continue as described in (6.4.2.).

### 6.5.2. Filtration method

Transfer the 500 ml of test solution (6.2.) or of the blank test solution (6.3.) into a 600 ml beaker.

Add, mixing after each addition, 10 ml of sulphuric acid (3.2.) and 25 ml of Fe(II) / Fe(III)-solution (3.4.). Allow to stand for 15 minutes.

Filter under vacuum through a membrane filter (4.3.) and wash twice with 15 ml of water (pH < 7).

Transfer the filter into a beaker containing 10 ml of the potassium hydroxide solution (3.3.) and dissolve the precipitate.

Transfer the solution into a 100 ml volumetric flask, add 10.0 g of sodium chloride (3.1.), dilute to 60 ml, mix and continue as described in (6.4.2.).

### 6.5.3. Photometric measurements

Carry out the photometric measurements of the two solutions obtained in (6.5.1.) or (6.5.2.) according to the instructions given in paragraph (6.4.3.).

## 7. EXPRESSION OF RESULTS

### 7.1. Evaluation

The hexacyanoferrate (II) content, expressed as  $[\text{Fe}(\text{CN})_6]$ , in mg/kg of salt, is given by the following equation

$$\text{Fe}(\text{CN})_6 = 0.502 \times \frac{500 \times (m_1 - m_0)}{m \times V}$$

or if expressed as  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ :

$$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O} = \frac{500 \times (m_1 - m_0)}{m \times V}$$

or if expressed as  $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ :

$$\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O} = 1.146 \times \frac{500 \times (m_1 - m_0)}{m \times V}$$

where

- $m$  is the mass in grams, of the test portion (6.1.),
- $m_1$  is the mass in micrograms, of hexacyanoferrate (II) expressed as  $[\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}]$ , analysed in the final solution (6.5.1.) or (6.5.2.) with the test solution,
- $m_0$  is the mass in micrograms, of hexacyanoferrate (II) expressed as  $[\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}]$ , analysed in the final solution (6.5.1.) or (6.5.2.) with the blank solution,
- $V$  is the volume, in millilitres, of test solution used in (6.5.1.) or (6.5.2.).

### 7.2. Repeatability and reproducibility

2011 (see ref. (1)):

20 participants analyzed 2 NaCl samples in triplicate applying their Prussian blue based method. The final result expressed in mean value and its 95 % confidence limit:

Sample 1 with a total of 30 observations:  $0.49 \pm 0.033$  mg  $\text{Fe}(\text{CN})_6$ - / kg of NaCl.

Sample 2 with a total of 42 observations:  $3.19 \pm 0.079$  mg  $\text{Fe}(\text{CN})_6$ - / kg of NaCl.

2014 (see ref. (2)):

18 participants analyzed 3 (spiked) brine samples in triplicate. This resulted in a repeatability limit  $r$ , reproducibility limit  $R$  at the overall level  $c$  in mg  $\text{Fe}(\text{CN})_6$ - / kg of NaCl obtained by  $k$  outlier-free participants:

<i>Brine prepared from</i>	<i>c</i>	<i>k</i>	<i>r</i>	<i>R</i>
Vacuum salt	473	10	13	66
Rock salt	78	14	4	12
Sea salt	55	14	4	13

## 8. REMARKS

**8.1.** Hexacyanoferrate (II) is determined simultaneously with hexacyanoferrate (III).

**8.2.** The intensity of the colour is dependant on the concentration of alkali metal present in the solution.

## 9. REFERENCES

- (1) AkzoNobel – M11056 (November 2011): Round robin study on Salt-2011; results, plots and statistics.
- (2) AkzoNobel – M2014271 (December 2014): Results of the round robin on YPS in brine prepared from vacuum, rock, sea salt.