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NATIONAL STANDARD OF THE PEOPLE'S REPUBLIC OF CHINA

GB/T 23950-2024

Replacing GB/T 23950-2009

General methods for the determination of heavy metals in inorganic chemical products

无机化工产品中重金属测定通用方法

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Table of Contents

4 General provisions and sample treatment

A warning at the head of the document notes that some of the reagents used are hazardous and call for care in handling, that users should have practical experience of proper laboratory work, that not every possible safety problem is identified, and that the user is responsible for adopting suitable safety and health measures and for meeting the conditions laid down in the relevant national regulations.

Clause 4 requires analytical grade reagents and the grade three water of GB/T 6682-2008

wherever no other requirement is noted, and impurity standard solutions, preparations and products made up according to HG/T 3696.2 and HG/T 3696.3 wherever nothing else is laid down. Clause 5 refers sample treatment to the method of 7.3 of GB/T 30902-2014. Clause 3 states that there are no terms to be defined for the purposes of the document.

6.1 Limit colour comparison method

The principle is that heavy metal ions in an inorganic chemical product form a coloured sulfide precipitate with divalent sulfide ion in a weakly acidic medium; where the heavy metal content is low the result is a stable brown suspension, which is compared with a standard colour solution prepared and treated at the same time and in the same way. The detection range of the method is 0.2 μg/mL to 2 μg/mL.

The reagents are hydrochloric acid solution 1+1, ammonia solution 1+14, an acetate buffer of pH about 3.5 made by dissolving 25.0 g of ammonium acetate in 25 mL of water, adding 45 mL of the hydrochloric acid solution, adjusting to pH 3.5 with the acid or the ammonia and diluting to 100 mL with water, saturated hydrogen sulfide water, sodium sulfide solution, a lead standard solution containing 0.01 mg of lead per millilitre made by diluting 1.00 mL of the lead stock solution of HG/T 3696.2 to 100 mL and kept refrigerated for one month, and phenolphthalein indicator at 10 g/L.

The test solution is prepared by weighing the sample as the product standard requires and treating it by the method suited to it under Clause 5; the treated solution is filtered if it is not clear, transferred in full to a 50 mL colour comparison tube and diluted to 25 mL with water; one drop of the phenolphthalein indicator is added and the solution brought to neutrality with the hydrochloric acid or the ammonia solution, that is to the point where the red colour has just gone or has just appeared; 5 mL of the acetate buffer is then added and the solution mixed.

The standard colour solution is made by taking the quantity of lead standard solution that answers to the heavy metal requirement of the product standard together with a suitable amount of matrix, the matrix being omitted where the test solution contains none or where its presence does not affect the determination, and treating it at the same time and in the same way as the test solution but without the sample solution. For the determination, 10 mL of freshly prepared saturated hydrogen sulfide water or 2 drops of sodium sulfide solution are added to the tube holding the test solution and to the tube holding the standard colour solution, water is added to the 50 mL mark, the tubes are shaken and left for 10 min, and the two colours are then compared against a white background, viewed from above and from the side.

6.2 Inductively coupled plasma optical emission spectrometry

The principle is that copper, zinc, cobalt, nickel, manganese, molybdenum, lead, titanium,

silver, arsenic, bismuth, cadmium, chromium, mercury, tin, vanadium, antimony and other heavy metal elements in inorganic chemical products are measured in nitric acid medium with an inductively coupled plasma optical emission spectrometer by the calibration curve method.

The reagents are nitric acid solution 1+1 made up from guaranteed grade reagent; a mixed standard solution containing 0.05 mg per millilitre each of copper, lead, zinc, cobalt, nickel, manganese, chromium, cadmium, bismuth, vanadium and arsenic; a second mixed standard containing 0.05 mg per millilitre each of molybdenum, antimony, titanium and tin; a silver standard solution and a mercury standard solution, each at 0.05 mg per millilitre. Each is made by pipetting 5 mL of the corresponding stock solutions prepared according to HG/T 3696.2 into a 100 mL volumetric flask, adding 4 mL of the nitric acid solution and diluting to the mark. The water used meets grade two of GB/T 6682-2008. The apparatus is an inductively coupled plasma optical emission spectrometer.

For the determination a suitable mass of sample is weighed according to the heavy metal requirement of the product standard and treated, and the calibration solutions and the test solution are prepared. The instrument conditions are optimised and the instrument warmed up and stabilised, and the measurement follows 7.4.3.1 of GB/T 30902-2014. A calibration curve is drawn for each element with the mass concentration of the calibration solutions in micrograms per millilitre on the horizontal axis and the spectral intensity on the vertical axis, and the concentration in the test solution is read off the curve from the measured intensity. Annex A gives the selectable wavelengths and the detection limits and Annex B the interferences and their elimination.

The heavy metal content is expressed as a mass fraction in milligrams per kilogram and is computed by Formula (1) from the sum over the elements of the concentration read from the calibration curve, which is taken as zero for an element not detected, the volume of the volumetric flask in millilitres, the mass of the sample in grams and the dilution factor, which is 1 where the sample has not been diluted. Under repeatability conditions the absolute difference between two parallel determinations shall not be greater than 15 percent of their arithmetic mean.

A Annexes A and B (informative)

Annex A gives, in Table A.1, the selectable wavelengths in nanometres and the detection limits in milligrams per litre for the elements determined by the plasma method, each element carrying one to three wavelengths. The table is set as two side by side blocks and the extraction merges the two blocks line by line, so the wavelengths and detection limits could not be assigned to their elements with certainty and the figures are not reproduced here.

B.1 deals with spectral interference, which comprises continuous background and line overlap. Matrix interference can be removed by optimising the test conditions and choosing

the best working parameters, and Table B.1 lists the main interfering elements at each selectable wavelength of each analyte. That table is set in the same two block layout as Table A.1 and its element, wavelength and interference triples could not be reproduced with certainty.

B.2 lists the ways of correcting interelement interference, to be chosen according to the case: chemical enrichment and separation, which improves the detectability of the element but is laborious and can introduce a reagent blank; matrix matching, in which standards are made up with a matrix like that of the sample, which removes the interference of a fixed matrix but depends on high purity reagents that are hard to obtain and makes the preparation of the standards laborious; background subtraction, in which the position and the manner of the subtraction are settled by experiment; and the interference coefficient method, in which a series of solutions of known interferent content is measured at the wavelength of the analyte, the combined content of interferent and analyte is compared with the two separate contents through Formula (B.1) to give the coefficient, and the correction is then made by hand or automatically by the instrument. The equation of Formula (B.1) is broken in the source and has not been reconstructed.

B.3 deals with non-spectral interference, which covers chemical, ionisation, physical and desolvation effects. Physical interference arises from the viscosity and the surface tension of the sample, and a high content of soluble salts or an excessive acidity will disturb the determination; such interference is removed by diluting the sample. Non-spectral interference is corrected by the internal standard method, which suppresses matrix interference: a fixed amount of an internal standard element is added to both the working standard solutions and the test solutions, the ratio of the intensity of the analyte to that of the internal standard is measured, and the correction curve is drawn against the concentrations of the working standard solutions for the quantification of the sample.