HJ

NATIONAL ENVIRONMENTAL PROTECTION STANDARD

OF THE PEOPLE'S REPUBLIC OF CHINA

HJ/T 83-2001

Water quality - Determination of adsorbable organic halogen - Ion chromatography method

水质　可吸附有机卤素(AOX)的测定　离子色谱法

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Foreword

The pre-treatment method (place the activated carbon absorbed with organics in high temperature furnace to burn, decompose, and transfer into inorganic halides) of water sample specified in this Standard is basically the same as ISO 9562:1989-09-01 and GB/T 15959-1995 "*Water quality - Determination of adsorbable organic halogens (AOX) - Microcoulometric method*", however, the detecting methods are different. This Standard specifies that using ion chromatography method to detect inorganic halogen ion that is produced and transferred from organic halogen. It can determine not only the total (in chlorine) of adsorbable organic halogens (AOX) in water, but also the adsorbable organic chlorine (AOCl), adsorbable organic fluorine (AOF) and adsorbable organic bromine (AOBr) in water.

Appendix A and appendix B in this Standard are normative.

This Standard shall be under the jurisdiction of General Administration of Environmental Protection - Science, Technology and Standard Division.

Drafting organization of this Standard: Shenyang Environmental Monitoring Center Station.

This Standard is first-time released, and it shall be implemented from April 1, 2002.

This Standard shall be interpreted by General Administration of Environmental Protection.

Water quality - Determination of adsorbable organic halogen (AOX) - Ion chromatography method

1 Subject content and scope

1.1 Subject content

This Standard specifies ion chromatography method that determines adsorbable organic halogen (AOX) in water.

1.2 Scope

This Standard applies to determine adsorbable organic halogen (AOX) in water and polluted water, including adsorbable organic chlorine (AOCl), adsorbable organic fluorine (AOF) and adsorbable organic bromine (AOBr).

When sample volume is between 50 and 200 ml, it can determine that the concentration range of adsorbable organic chlorine (AOCl) is 15~600 μg/L, the concentration range of adsorbable organic fluorine (AOF) is 5~300 μg/L, and the concentration range of adsorbable organic bromine (AOBr) is 9~1200 μg/L.

1.3 Interference and elimination

1.3.1 Inorganic halogen ion in water, during the sample enrichment process, also can partly remain in activated carbon to interfere the determination. Use 20 ml of washing liquid of acidic sodium nitrate (4.12) to leach the activated carbon adsorption column, so that the interference can be eliminated entirely.

1.3.2 When there are insoluble chloride and biological cells (such as microorganism and alga) etc. in the water sample, the determination result will be higher; use nitrate (4.9) to adjust the pH value to be within 1.5~2.0; analyze it after 8 h.

1.3.3 When there is active chlorine in the water sample, the determination result of AOCl will be higher. Add 5 ml of sodium sulfite solution (4.8) immediately in 100 ml of water sample, after sampling.

2 Definitions

2.1 adsorbable organic halogen (AOX)

It refers to the total (calculated by Cl) of halogen elements (including fluorine, chlorine and bromine) which can be adsorbed by activated carbon and can be combined on the

organic compound, under the conditions specified by this Standard.

2.2 adsorbable organic chlorine (AOCl)

It refers to the total of chlorine which can be adsorbed by activated carbon and can be combined on the organic compound, under the conditions specified by this Standard.

2.3 adsorbable organic fluorine (AOF)

It refers to the total of fluorine which can be adsorbed by activated carbon and can be combined on the organic compound, under the conditions specified by this Standard.

2.4 adsorbable organic bromine (AOBr)

It refers to the total of bromine which can be adsorbed by activated carbon and can be combined on the organic compound, under the conditions specified by this Standard.

3 Method and principle

Use activated carbon to adsorb the organic halogen compounds in water; place the active carbon that have adsorbed organics into high temperature furnace to burn, decompose, and transfer into hydrogen halide (hydride of fluorine, chlorine and bromine); use ion chromatography method to separate and determine, after absorbed by alkaline solution.

4 Reagents and materials

Unless otherwise stated, when analyzing, distilled water free from organics and analytically pure reagents complying with national standards shall be used.

4.1 distilled water free from organics: use glass distiller to distill deionized water that has been filtered by activated carbon (4.2) column; distill it before using.

4.2 Activated carbon: analytically pure, 20~60 meshes.

4.3 Purified activated carbon for adsorption use (appendix A).

4.4 Oxygen (O_2): 99.9% (V/V).

4.5 5% potassium permanganate solution (m/V).

4.6 10% sodium hydroxide solution (m/V).

4.7 High-purity nitrogen (N_2): 99.99% (V/V).

4.8 Sodium sulfite solution, $c(Na_2SO_3)$=0.2 mol/L.

7.2.2.1 Adsorption

According to 5.4.1, stuff the activated carbon adsorption column; connect the adsorption device; take 25~200 ml of preheated water sample (6) according to the organic contents in the samples; add 5 ml of sodium nitrate stock solution (4.11) in every 100 ml of water sample; at this moment, the pH value of water sample shall be less than 2. Otherwise, add nitrate (4.9) to adjust. Move water sample to sample tube of adsorption device; plug a cover for sealing; adjust nitrogen pressure to let the water sample to flow past the adsorption column at the speed of 2~3 ml/min. Add 20 ml of washing liquid of sodium nitrate (4.12) at the speed of 2~3 ml/min to wash the adsorption column. Also, simple adsorption device (5.4.2) can be used instead of above steps.

7.2.2.2 Combustion

Preheat up the burner and maintain the temperature at 950±10°C.

Adjust the oxygen pressure and flowmeter to make the speed of blowing oxygen toward the combustion tube's inner tube to be 120~150 ml/min, and the speed toward outer tube be 40~60 ml/min.

Connect the gas-bubble absorption tube (5.6) that contains 3.00 ml of borax absorbing liquid (4.19) to the outlet of combustion tube; use the asbestos cloth to wrap the junction to avoid moisture condensation.

Open the silica gel plug at the sample-inlet of combustion tube; use flattened pinhead (5.9) to move the wet activated carbon that has adsorbed sample in the activated carbon adsorption column to alumina boat, then plug it.

Push the alumina boat to the preheated zone (furnace's mouth) of combustion tube; stay for 2 min; push the alumina boat slowly to the high temperature zone; after 3 min, pull it out to the sample-inlet. Continue to blow oxygen for 4~5 min.

7.2.2.3 Measurement

Take down the absorption tube and connecting tube from combustion system; use rubber pipette bulb to blow oxygen from the outlet of absorption tube (Note: do not blow out the absorbing liquid from bottle), and wash repeatedly to let the fog-drops at absorption tube's inlet and in connecting tube to enter into the absorption tube.

Use ion chromatograph to measure the contents of Cl^-, F^- and Br^- in the absorption tube.

7.3 Determination of full-procedure blank samples

Use distilled water to replace the sample; conduct the full-procedure blank test according to the steps same as that of sample determination.

curve, mg/L.

8.3 Concentration calculation of adsorbable organic bromine (AOBr) in water:

$$c_{(AOBr)} = \frac{(C_{Br} - C_{0Br})V_2 D}{V_1}$$

Where:

$c_{(AOBr)}$ - the concentration of adsorbable organic bromine (AOBr) in water, μg/L;

c_{Br} - Br^- concentration in the sample that is found from the standard curve, mg/L;

c_{0Br} - Br^- concentration in the blank sample (7.3) that is found from the standard curve, mg/L.

8.4 Concentration calculation of adsorbable organic halogen (AOX) in water:

$$c_{(AOX)} = c_{(AOCl)} + 1.866c_{(AOF)} + 0.444c_{(AOBr)}$$

Where:

$c_{(AOX)}$ - the concentration of adsorbable organic halogen (AOX) in water, μg/L;

1.866 - the coefficient converted from fluorine to chlorine;

0.444 - the coefficient converted from bromine to chlorine.

8.5 Concentration calculation of volatile organic halogen in water:

$$\begin{aligned} c_{(VOX)} &= c_{(VOCl)} + 1.866c_{(VOF)} + 0.444c_{(VOBr)} \\ &= [(c_{Cl} - c_{0Cl}) + 1.866(c_F - c_{0F}) + 0.444(c_{Br} - c_{0Br})]DV_2 / V_3 \end{aligned}$$

Where:

$c_{(VOX)}$ - the concentration of volatile organic halogen in water, μg/L;

$c_{(VOCl)}$ - the concentration of volatile organic chlorine in water, μg/L;

$c_{(VOF)}$ - the concentration of volatile organic fluorine in water, μg/L;

10.2 Common oxygen and medical oxygen contain trace impurities which will interfere the determination, so that the full-procedure blank value will be higher and unstable. It can be used after purifying by purification device (5.3).

10.3 Every batch of samples shall at least carry out two full-procedure blank tests (7.3) and verification of full-analysis steps (7.4). The absolute value of the difference between the recovery value of adsorbable organic chlorine (AOCl) and expected value shall not be more than 15% of expected value. If not, check the water, reagents, combustion system and the full-analysis steps.

10.4 When adsorbing water sample by adsorption device of nitrogen pressure, open the exhaust valve to adjust the nitrogen flow to be 0.1~0.2 ml/min; close the exhaust valve to pressure the water sample after the flow is stable. Avoid excessive pressure and adsorption tube detachment.

10.5 When using activated carbon to adsorb water sample with unknown concentration, take different volumes of water sample (such as: 50 ml and 100 ml) to respectively adsorb; check whether the adsorption is complete. If the measured concentration value of the sample that has smaller volume IS 15% higher than the sample that has bigger volume, it shall be re-adsorbed after diluting the water sample.

10.6 Use (1+2) nitrate to soak the used gas-bubble absorption tube over night; use water to wash; it may be reused after using deionized water to wash cleanly.

Appendix B

(Standard)

Preparation of purified activated carbon

B1 Preparation method

Use the grinding sieve of which the hole diameter is 125~177 μm (80~120 mesh) to analyze pure activated carbon; use 1 mol/L nitric acid solution (5.10) to soak for more than 12 h; move to microporous membrane filter (5.5); use water to wash until it is free from nitrate ions (use sulfuric acid solution of diphenylamine to check until there is no dark-blue substance is produced); dry it; under the protection of nitrogen-stream, heat at 450~500°C for more than 3 h; cool down to room temperature. Use the sieve of which the hole diameter is 105~149 μm (100~140 order), in indoor condition where is clean and without pollution of organic halogen compounds, to purify the activated carbon; respectively take the amount used for the same-day to place into small glass bottles (2~5 ml), seal and preserve. Open before it is used.

B2 Purity test

According to the steps (7.3) specified in this Standard, determine the full-procedure blank value of activated carbon after purifying. Determination value of adsorbable organic chlorine (AOCl) is less than 35 μg/L; the within-batch standard deviation that is repeatedly determined (m=4, n=4) by 4 laboratories is less than 5 μg/L. The full-procedure blank value of AOF is less than 11 μg/L; the within-batch standard deviation that is repeatedly determined (m=4, n=4) by 6 laboratories is less than 2 μg/L. The full-procedure blank value of AOBr is zero.

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