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TEST METHOD FOR THE TOTAL CONTENT OF NON-VOLATILE PHENOLS IN WASTEWATER

I. JOHANNES
L. MÖLDER
L. TIIKMA

Institute of Chemistry,
Tallinn Technical University
15 Akadeemia St., Tallinn
12618 Estonia

An instruction for testing of the total content of non-volatile by steam phenols (resorcinol and naphthol alkyl derivatives) in water is given. The colorimetric method is based on the formation of red cobalt complexes specially with nitrosated resorcinol and naphthol series phenols when sodium nitrite and cobalt sulphate are added to the slightly acidic sample.

Test Method I regards co-existence of phenolic compounds which can be subjected to mono- and dinitroso substitutions and subsequently give two types of cobalt complexes. Test Method II reports the test results as 2,5-dimethylresorcinol.

1. Introduction

According to the legislation of Estonian Government [1], the pollution charges for total phenolic contamination, including mono- and dihydric phenols, are 10,518 Estonian kroons per tonne.

Monohydric phenols are more toxic than dihydric ones. Consequently, the pollution charges for the two series of phenols should be differentiated. The existing equalisation is motivated by the absence of any appropriate selective test method for dihydric phenols.

The HPLC method described in [2] is selective and sensitive, but underestimates the total phenolic contamination due to the lack of standards for several tens unusual dihydric phenols specific to wastewater of kukersite retorting, mainly alkyl derivatives of 1,3-benzenediol (resorcinol).

Up to the present, the total content of monohydric hydroxybenzene series phenols, so called volatile (by steam) phenols, is estimated using

the well-known colorimetric method with 4-aminoantipyrine [3]. The procedure involves first separating the steam distillable monohydric phenols from the background matrice by distillation. The result is reported as hydroxybenzene, so-called phenol index. Due to the different boiling points and colorimetric extinction coefficients of individual volatile phenols, the total result depends on the pollution composition.

The total content of dihydric phenols, so-called non-volatile phenols, when being tested at all, is found subtracting the total content of volatile phenols from the overall content of phenolic compounds. The latter is estimated by the colour reaction of 4-nitroaniline with phenolic compounds in the initial sample [4]. The result, like on the volatile phenols, depends on the composition of the phenolic pollution. The mistakes made by estimation of the overall and total volatile phenols may significantly increase when the total content of non-volatile phenols is found as their difference.

We have proposed a new selective colorimetric method for direct determination of non-volatile phenols [5, 6]. The method is based on the formation of red cobalt complexes with aromatic compounds, which have NO, and OH substituents in *ortho*-positions. Such a substitution is specific for resorcinol and naphthol series phenols, the main non-volatile phenols produced by kukersite retorting. Moreover, monohydric phenols form *para*-nitroso products and do not interfere. Oils, resins and other compounds present in wastewater do not interfere because they cannot be nitrosated with such a weak agent as HNO_2.

The method regards the formation of two different types of complexes:

(1) CoA_3 where A is a ligand consisting of a single NO substituent, a typical nitrosation product of resorcinol 2-alkyl and 2,4- or 2,5-dialkyl derivatives

(2) CoB_2 where B is a ligand consisting of two NO substituents, a typical nitrosation product of resorcinol and resorcinol 4- or 5-alkyl derivatives

Different absorption factors of CoA_3 and CoB_2 are taken into account testing the optical density of samples under two conditions.

We have tested numerous water samples from the ash dump drenage leachate, channel systems and the rivers Kohtla and Purtse. In these samples, the content of non-volatile phenols found counting the co-existence of CoB_2 and CoA_3 is equal to that of only CoA_3. This fact suggests that in the open air degradation deactivates the second nitroso substitution at the phenolic compounds for the type (2). For example, dimerization would take place. So, mainly the type of complexes CoA_3 can form. As a result, the procedure for determination of non-volatile phenols in environmental samples can be simplified.

The aim of this paper is to give a comprehensive instruction for colorimetric determination of (1) the total content of non-volatile phenols and (2) the same reported as 2,5-dimethylresorcinol (2,5-dimethylresorcinol index).

2. Scope

2.1. The test method describes a colorimetric determination of total content for 0.1-2 mg/L level of non-volatile by steam phenols in water samples. Higher levels can be determined by dilution.

2.2. The test method addresses a specific application as follows:

- Method I - for any water sample
- Method II - an express method for wastewater except freshly prepared standard solutions containing phenolic compounds which form the complex CoB_2

3. Summary of Test Method

By addition of cobalt sulphate and sodium nitrite to the slightly acidic sample (pH 4-5) resorcinol and naphthol series phenols are converted to *ortho*-nitroso-hydroxy compounds and subsequently to cobalt complexes.

To avoid degradation of nitrosated compounds by the excess of nitrite demanded cobalt sulphate must be added before nitrite. The absorbance of the cobalt complexes formed is measured on a photometer under two conditions using two standards when Method I is followed. Only the optimum conditions for formation of CoA_3 and a single standard are required when Method II is followed. The content of non-volatile phenols is expressed in terms of milligrams per litre.

4. Interferences

Any suspended matter must be removed by centrifugation or filtration.

Interference by other dissoluted compounds is negligible. Hydroxybenzene series phenols form *para*-nitrosated products and therefore cannot form cobalt complexes.

Oils, resins, alkanes, alkenes and non-phenolic aromatic compounds (except aromatic amines) cannot react with the weak nirosating agent, HNO_2.

It is the user's responsibility to insure the validity of these test methods for water of untested matrices.

5. Apparatus

5.1. Spectrophotometer suitable for use at 420 and 450 nm (Test Method I) or at 420 nm (Test Method II) with adsorption cells, having 50 mm path length. If the absorbance is greater than 1.0, the smaller size cells can be used.

5.2. Volumetric flasks 1000 mL for reagents A, B and C, and 500, 250, 200 and 50 mL for standard solutions.

5.3. Measuring pipettes 1, 2, 10, 20 (30, 40) mL.

5.4. Beakers 50-100 mL.

6. Reagents

6.1. Reagent grade chemicals should be used in all tests. Other grades may be used, provided it is first ascertained that the reagent does not less the accuracy of the determination.

6.2. Reagent A (0.02 M cobalt sulphate in acetic acid - acetate buffer). Dissolve in water and dilute to 1 litre of:

- Cobalt sulphate ($CoSO_4 \cdot 7H_2O$) - 5.6 g
- Glacial acetic acid (CH_3COOH) - 60.5 g (57.6 mL)
- Sodium acetate ($CH_3COONa \cdot 3H_2O$) - 129 g

6.3. Reagent B (2 M sodium nitrite). Dissolve 138 g of sodium nitrite ($NaNO_2$) in water and dilute to 1 litre.

6.4. Reagent C (0.5 M sodium nitrite). Dissolve 34.5 g of sodium nitrite ($NaNO_2$) in water and dilute to 1 litre (Test Method I only).

6.5. 2,5-Dimethylresorcinol, stock (1 g/L 2,5-DMR). Dissolve 0.500 g of 2,5-DMR in freshly boiled and cooled water. Dilute to 500 mL with freshly boiled and cooled water.

6.6. 2,5-Dimethylresorcinol, standard (20 mg/L 2,5-DMR). Dilute 5 mL of the stock **6.5** to 250 mL with freshly boiled and cooled water.

6.7. 5-Methylresorcinol (orcinol), stock (1 g/L 5-MR). Dissolve 0.500 g of 5-MR or 0.5726 g of 5-MR $\cdot H_2O$ in freshly boiled and cooled water. Dilute to 500 mL with freshly boiled and cooled water.

6.8. 5-Methylresorcinol, standard (10 mg/L 5-MR). Dilute 2 mL of the stock **6.7** to 200 mL with freshly boiled and cooled water.

The reagents A (**6.2**), B (**6.3**) and C (**6.4**) are stable in time. Fresh stock solutions (**6.5** and **6.7**) must be prepared whenever the solutions become yellowish or tawny (within 2-3 weeks). Fresh standard solutions (**6.6** and **6.8**) must be prepared on the day of use.

7. Calibration

7.1. 2,5-Dimethylresorcinol. Prepare a series of standards transferring 0, 1, 2, 3, 4, and 5 mL of the standard (**6.6**) into 50-mL volumetric flasks. Dilute to 50 mL with distilled water. The concentrations in the series of standards are 0, 0.4, 0.8, 1.2, 1.6, and 2.0 mg/L of 2,5-dimethylresorcinol respectively.

7.1.1. Graph for 2,5-DMR(420). Transfer 20 mL of the series of standards (**7.1**) to beakers about 50-100 mL. Add 2.0 mL of Reagent A (**6.2**) and 1.0 mL of Reagent B (**6.3**). Mix immediately. After 60 min record the optical density of the solutions at 420 nm, E(420), against the zero optical density of the first solution which does not contain 2,5-dimethylresorcinol. Find the slope (tangent), $B_{2,5\text{-DMR}}(420)$, for the plot of $E(420)$ versus the concentrations of the series of standards.

7.1.2. Graph for 2,5-DMR(450). (For Method I only). Transfer 20 mL of the series of standards (**7.1**) to beakers about 50-100 mL. Add 2.0 mL of Reagent A (**6.2**) and 1.0 mL of Reagent C (**6.4**). Mix immediately. After 60 min record the optical density of the solution at 450 nm, $E(450)$, against the zero optical density of the first solution which does not contain 2,5-dimethylresorcinol. Find the slope (tangent), $B_{2,5\text{-DMR}}(450)$, for the plot of $E(450)$ versus the concentrations of the series of standards.

7.2. 5-Methylresorcinol. (For Method I only). Prepare a series of standards transferring 0, 1, 2, 3, 4 and 5 mL of the standard (**6.8**) into 50-mL volumetric flasks. Dilute to 50 mL with distilled water. The concentrations of the series of standards are 0, 0.2, 0.4, 0.6, 0.8, and 1.0 mg/L 5-methylresorcinol respectively.

7.2.1. Graph for 5-MR(420). Transfer 20 mL of the series of standards (**7.2**) to beakers about 50-100 mL. Add 2.0 mL of Reagent A (**6.2**) and 1.0 mL of Reagent B (**6.3**). Mix immediately. After 60 min record the optical density of the solutions at 420 nm, $E(420)$, against the zero optical density of the first solution which does not contain 5-methylresorcinol. Find the slope (tangent), $B_{5\text{-MR}}(420)$, for the plot of $E(420)$ versus the concentrations of the series of standards.

7.2.2. Graph for 5-MR(450). Transfer 20 mL of the series of standards (**7.2**) to beakers about 50-100 mL. Add 2.0 mL of Reagent A (**6.2**) and 1.0 mL of Reagent C (**6.4**). Mix immediately. After 60 min record the optical density of the solutions at 450 nm, $E(450)$, against the zero optical density of the first solution which does not contain 5-methyl-

resorcinol. Find the slope (tangent), $B_{5\text{-MR}}(450)$, for the plot of E versus the concentrations of the series of standards.

8. Test Method I

8.1. Procedure for Samples

8.1.1. Transfer into two about 50-100 mL beakers 20 mL of the sample being tested, or a suitable aliquot diluted to 20 mL containing no more than 2 mg/litre of total non-volatile phenols. Trial and error tests may be necessary to determine the volume of a suitable aliquot.

8.1.2. Add to the sample in the first beaker 2.0 mL of Reagent A (**6.2**) and 1.0 mL of Reagent B (**6.3**). After 60 min, record the optical density of the sample at 420 nm, $E(420)$.

8.1.3. Add to the sample in the second beaker 2.0 mL of Reagent A (**6.2**) and 1.0 mL of Reagent C (**6.4**). After 60 min, record the optical density of the sample at 450 nm, $E(450)$.

8.2. Calculation

8.2.1. Calculate the total content of non-volatile phenols, milligrams per litre, X, as follows:

$$X = 20[p\text{E}(420) - q\text{E}(450)]/V$$

where V is the volume of the primary sample present in 20 mL.

Calculate the coefficients p and q using the slopes of Graphs (**7.1.1, 7.1.2, 7.2.1** and **7.2.2**) as follows:

$$p = [B_{5\text{-MR}}(450) - B_{2,5\text{-DMR}}(450)]/\Delta;$$

$$q = [B_{5\text{-MR}}(420) - fB_{2,5\text{-DMR}}(420)]/\Delta;$$

$$\Delta = fB_{2,5\text{-DMR}}(420)\, B_{5\text{-MR}}(450) - B_{5\text{-MR}}(420)\, B_{2,5\text{-DMR}}(450)$$

Note: The factor f corrects the difference between $B_{2,5\text{-DMR}}(420)$ and the mean slope of the graphs for the phenolic components in the sample, which form the complex CoA_3. When 2,5-dimethylresorcinol is applied as the standard for the blend of kukersite oil shale originated phenols, f = = 0.894 [6]. It is the users responsibility to insure the validity of this factor for water of another origin.

9. Test Method II: 2,5-Dimethylresorcinol Index (Express Method for Wastewater Samples)

9.1. Procedure for samples is the same as in **8.1.1** and **8.1.2**

9.2. Calculation. The total concentration of non-volatile phenols in wastewater samples, Y, milligrams per litre, is calculated as follows:

$$Y = 20E(420)/[VB_{2,5\text{-DMR}}(420)]$$

where V and $B_{2,5\text{-DMR}}(420)$ are the same as in **8.2** and **7.1.1**.

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